

INERT ANODE AND ELECTROLYTE CONTROL

INCORPORATION BY REFERENCE

- 5 [0001] A PCT Request Form is filed concurrently with this specification as part of the present application. Each application that the present application claims 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

- 10 [0002] Electroplating is a technique commonly used in the fabrication of semiconductor devices. For instance, electroplating may be used to deposit one or more conductive material such as a metal or a metallic alloy on a semiconductor substrate. One such material that may be deposited is copper. Other example materials include, but are not limited to, aluminum, nickel, iron, cobalt,
15 zinc, tin, silver, gold, metal alloys, and combinations thereof. While much of the present disclosure is focused on examples where the material being deposited is copper, it should be understood that the invention is not so limited. The examples herein may be practiced in the context of electroplating any type of metal, with any time of solvent (e.g. water, dimethylsulfoxide, molten salts), and electrolytes, as desired for a particular application.
- 20 [0003] The background description provided herein is for the purposes of generally presenting the context of the disclosure. Work of the presently named inventors, to the extent it is described in this background section, as well as aspects of the description that may not otherwise qualify as prior art at the time of filing, are neither expressly nor impliedly admitted as prior art against the present disclosure.

SUMMARY

- 25 [0004] Various examples herein relate to methods, apparatus, and systems for electroplating one or more metals on a semiconductor substrate. Advantageously, the techniques described herein achieve stable electrolyte composition control even with the use of an inert anode.
- 30 [0005] In one aspect of the disclosed examples, a system for electroplating a metal on a substrate is provided, the system including: an electroplating cell including: an anode, where the anode is an inert anode, a cathode chamber configured to hold catholyte and receive the substrate during electroplating such that the substrate is exposed to the catholyte, an anode chamber configured to hold anolyte and the anode during electroplating, a membrane configured to separate the cathode

chamber from the anode chamber, where the membrane permits passage of ions from the anode chamber to the cathode chamber during electroplating and prevents passage of organic compounds from the cathode chamber to the anode chamber during electroplating; and dosing hardware configured to provide a metal-containing material to the anolyte, where the metal-containing material is a heterogeneous material including the metal being electroplated on the substrate.

[0006] In some examples, the metal-containing material includes a metal oxide, a metal hydroxide, a metal carbonate, a metal bicarbonate, a metal sulfide, or a combination thereof.

[0007] In some examples, the system further includes a filter, where the filter is configured to remove the metal-containing material from the anolyte. In these or other examples, the dosing hardware includes a mixing tank in fluidic communication with the anode chamber and a mixer for fluidizing the metal-containing material within the mixing tank. In some such examples, the system further includes a trunk line configured to deliver a slurry including the anolyte and the metal-containing material from the mixing tank toward the anode chamber. In these or other examples, the system includes a plurality of distinct electroplating apparatuses, each having at least one electroplating cell, where the trunk line is configured to deliver the slurry to the plurality of distinct electroplating apparatuses.

[0008] The electroplating cell may be located in a particular area, and/or may have a particular relative position with respect to other components in the system. For instance, in some examples the electroplating cell is positioned in a clean room of a semiconductor fabrication facility, and the mixing tank is positioned either (i) outside of the clean room of the semiconductor fabrication facility, or (ii) within a sub-environment within the clean room of the semiconductor fabrication facility, where the sub-environment includes a filter that enables use of powdered material within the sub-environment without contaminating the rest of the clean room.

[0009] In various examples, the system further includes a controller configured to cause introduction of the metal-containing material to the anolyte. In some such examples, the system further includes a mixing tank in fluidic communication with the anode chamber, and the dosing hardware is configured to add the metal-containing material to the anolyte in the mixing tank, where the mixing tank includes a level sensor for sensing a level of anolyte in the mixing tank, and where the controller is configured to cause introduction of the metal-containing material from the dosing hardware to the anolyte in the mixing tank based at least in part on input from the level sensor on the mixing tank.

[0010] In various examples where the system includes a filter, the system may further include a differential pressure sensor configured to measure a pressure differential between anolyte entering the filter and anolyte exiting the filter.

[0011] In various examples, the system includes a plurality of electroplating cells and one or more anolyte reservoir.

[0012] In various examples, the dosing hardware includes a cartridge including the metal-containing material therein, where the cartridge is configured to receive anolyte and expose the anolyte to the metal-containing material. In some such examples, the metal-containing material includes porous media formed by sintering one or more metal-containing powder.

[0013] In some examples, the system further includes a second membrane positioned below the membrane, where the second membrane permits passage of ions from the anode chamber to the cathode chamber during electroplating and prevents passage of organic compounds from the cathode chamber to the anode chamber during electroplating; and a middle chamber positioned below the membrane and above the second membrane, between the cathode chamber and the anode chamber, where an inlet of the dosing hardware is configured to receive anolyte flowing from the anode chamber, and an outlet of the dosing hardware is configured to deliver anolyte flowing toward the middle chamber.

[0014] In another aspect of the disclosed examples, a method of electroplating a metal onto a substrate is provided, the method including: providing the substrate in an electroplating cell, the electroplating cell including: an anode, wherein the anode is an inert anode; a cathode chamber configured to hold catholyte and receive the substrate during electroplating such that the substrate is exposed to the catholyte, an anode chamber configured to hold anolyte and the anode during electroplating, a membrane separating the cathode chamber from the anode chamber, where the membrane permits passage of ions from the anode chamber to the cathode chamber during electroplating and prevents passage of organic compounds from the cathode chamber to the anode chamber during electroplating; oxidizing the anolyte at the anode to generate hydrogen ions; electroplating the metal onto the substrate; and exposing the anolyte to a metal-containing material, the metal-containing material including a heterogeneous material including the metal being electroplated on the substrate, where exposing the anolyte to the metal-containing material reacts the hydrogen ions generated at the anode with the metal-containing material to produce metal ions in the anolyte.

[0015] In some examples, the metal-containing material includes a metal oxide, a metal hydroxide, a metal carbonate, a metal bicarbonate, a metal sulfide, or a combination thereof.

[0016] In various examples, the method further includes filtering the anolyte to remove the metal-containing material from the anolyte. In these or other examples, the method may further include adding the metal-containing material to a mixing tank in fluidic communication with the anode chamber. In some such examples, the method further includes flowing a slurry of the

anolyte and the metal-containing material in a trunk line from the mixing tank toward the anode chamber.

[0017] The electroplating cell may be located in a particular area, and/or may have a particular relative position with respect to other components in the system. For instance, in some examples the electroplating cell is positioned in a clean room of a semiconductor fabrication facility, and the mixing tank is positioned either (i) outside of the clean room of the semiconductor fabrication facility, or (ii) within a sub-environment within the clean room of the semiconductor fabrication facility, where the sub-environment includes a filter that enables use of powdered material within the sub-environment without contaminating the rest of the clean room.

[0018] In some examples, the method further includes measuring a level of anolyte in the mixing tank with a level sensor, and adding the metal-containing material to the mixing tank based at least in part on the measured level of anolyte in the mixing tank. In these or other examples, the method may further include flowing the anolyte through a filter, and sensing a differential pressure between anolyte entering the filter and anolyte exiting the filter.

[0019] In some examples, exposing the anolyte to the metal-containing material comprises flowing the anolyte through a cartridge comprising the metal-containing material.

[0020] In a further aspect of the disclosed examples, a system for electroplating a metal on a substrate is provided, the system including: an electroplating cell including: a cathode chamber configured to hold catholyte and receive the substrate during electroplating such that the substrate is exposed to the catholyte, an anode chamber configured to hold anolyte and an anode during electroplating, a membrane separating the cathode chamber from the anode chamber, where the membrane permits passage of ions through the membrane during electroplating, and the anode, where the anode is an inert anode; and a controller configured to cause: exposing the anolyte to a metal-containing material, the metal-containing material including a heterogeneous material including the metal being electroplated on the substrate, to thereby react hydrogen ions generated at the anode with the metal-containing material to generate metal ions in the anolyte.

[0021] These and other aspects are described further below with reference to the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] FIG. 1A presents a view of an electroplating cell having an active (e.g., soluble) anode.

[0023] FIG. 1B presents a view of an electroplating cell having an inert (e.g., insoluble) anode.

[0024] FIG. 1C presents a view of an electroplating cell having an inert anode and an ion exchanger.

[0025] FIG. 1D presents a view of an electroplating cell similar to the one shown in FIG. 1C,

including an additional membrane that may operate to further reduce unwanted proton migration.

[0026] FIGS. 1E and 1F illustrate examples of ion exchangers.

[0027] FIGS. 2A-2C present modeling results showing the concentration of copper and acid over time in the electroplating cells shown in FIGS. 1A-1C, respectively.

5 [0028] FIG. 3 depicts an electroplating system having both an anolyte recirculation loop and a catholyte recirculation loop according to an example herein.

[0029] FIG. 4 illustrates an electroplating system where an electroplating apparatus provides a common anolyte reservoir and contact unit that are shared among several electroplating cells.

10 [0030] FIG. 5 illustrates an electroplating system where an electroplating apparatus provides separate anolyte reservoirs and contact units for each individual electroplating cell therein.

[0031] FIG. 6 illustrates an electroplating system where a number of electroplating apparatuses are configured to interact with a shared metal-containing material fluidization equipment.

[0032] FIG. 7 depicts an electroplating cell according to certain examples.

15 [0033] FIG. 8 depicts an electroplating apparatus having a number of electroplating cells therein according to certain examples.

DETAILED DESCRIPTION

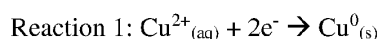
[0034] In the following description, numerous specific details are set forth to provide a thorough understanding of the presented examples. The disclosed examples may be practiced without some
20 or all of these specific details. In other instances, well-known process operations have not been described in detail to not unnecessarily obscure the disclosed examples. While the disclosed examples will be described in conjunction with the specific examples, it will be understood that it is not intended to limit the disclosed examples.

[0035] Control of the composition and concentration of the electroplating solution used in an
25 electroplating system may be important to the performance of the electrochemical deposition process. Typically, there are multiple components in a given electroplating solution. For example, the composition of electroplating solution used for the deposition of copper on a semiconductor substrate can vary, but may include, e.g., sulfuric acid, a copper salt, chloride ion, and a mixture of organic additives that may be provided to promote bottom-up fill, surface smoothness, grown
30 feature flatness, or another desired type of plating behavior.

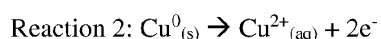
[0036] In many cases, it is desirable to separate an electroplating cell into different regions using a semi-permeable membrane. These regions can include a cathode chamber where the substrate is positioned during electroplating, and an anode chamber (often referred to as a separated anode chamber) where the anode is situated. This separation of anodic and cathodic regions of an

electroplating cell by a semi-permeable membrane can be beneficial because chemical processes occurring at the anode and at the cathode during electroplating may not be compatible. For example, during operation, insoluble particles may form on the anode. Protection of the substrate from such insoluble particles is desirable to avoid interference of the particles with subsequent metal deposition processes conducted on the substrate. Also, the restriction of organic additives to the cathode chamber may be desirable to prevent such additives from contacting and/or reacting with the anode. A suitable membrane allows for the flow of ions, and hence, current, between the anodic and cathodic region of the plating cell, but still restricts unwanted particles and/or organic additives from passing through the membrane. Thus, usage of the membrane during electrodeposition will result in different chemical environments in the cathode chamber compared to the anode chamber. Electrolyte contained in the anode chamber may be referred to as the “anolyte.” Likewise, electrolyte contained in the cathode chamber may be referred to as the “catholyte.”

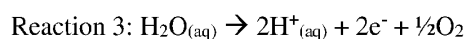
[0037] During electroplating, consumption of soluble, reducible species occurs at the substrate, which acts as a cathode. In the context of plating copper for example, the reaction at the substrate may occur according to Reaction 1:



[0038] A complementary reaction occurs at the anode to complete the circuit. The complementary reaction involves oxidizing either the anode itself or the electrolyte/water surrounding the anode. In cases where the anode itself is oxidized, the anode may be referred to as an active anode, a soluble anode, or a consumable anode. In the context of plating copper using an active anode, the reaction at the anode may occur according to Reaction 2:



[0039] In cases where the water surrounding the anode is oxidized, the anode may be referred to as an inert anode, a dimensionally stable anode, or an inactive anode. The “inert” descriptor reflects the fact that water and/or some other oxidizable component in the electrolyte is being consumed, rather than the anode itself (e.g., the anode electrode itself isn’t oxidized, but facilitates an oxidation reaction of an anolyte component). As an example of an alternative oxidizing component, ferrous ion (Fe^{+2}) may be caused to react to form ferric ion (Fe^{+3}) as the dominant anode oxidation reaction instead of water. Typically, the alternative oxidizing component will have a lower (less positive) oxidizing potential than water for it to replace water oxidation as the primary reaction. In the context of plating copper using an inert anode, the reaction at the anode may occur according to Reaction 3:



[0040] FIG. 1A presents a view of an electroplating cell 101 having an active anode 102, while FIG. 1B presents a view of an electroplating cell 121 having an inert anode 122. In both examples, the electroplating cell 101 or 121 includes a membrane 105 that separates the electroplating chamber into a cathode chamber 106 where a substrate 103 is positioned, and an anode chamber 107 where the anode (e.g., active anode 102 or inert anode 122) is positioned.

[0041] The anode is often a solid mass of metal. An active anode includes the same metal that is being plated on the substrate. For instance, in the context of electroplating copper using an active anode 102 as shown in FIG. 1A, the active anode 102 would be composed of copper (or a copper-containing material such as phosphorus-doped copper), and the reaction occurring at the anode is Reaction 2. By contrast, an inert anode is composed of an auxiliary metal that is resistant to oxidative corrosion, and can support an anodic reaction involving the breakdown of abundant electrolyte or solvent (e.g., water, as shown in Reaction 3). In many cases, these auxiliary metals are provided in the form of catalytically active precious metal oxides. In the context of electroplating copper using an inert anode 122 as shown in FIG. 1B, the inert anode 122 may be composed of one or more materials selected from the group consisting of platinum, gold, palladium, titanium, tungsten, tantalum, molybdenum, ruthenium, niobium, iridium, etc. Combinations and/or oxidized forms of these materials may also be used. In various cases, the inert anode 122 may include a base metal current collector that is noble to oxidation in water (e.g., Pt, Au, Pd), or a base metal current collector that forms an oxide film that passivates against corrosion (e.g., Ti, W, Ta, Mo). In various examples, the inert anode may optionally include a surface coating that is an electro-catalyst for water oxidation (e.g., Pt, RuO₂, NbO₂, IrO₂). A widely commercially available type of inert anode is referred to as a MMO inert anode which is a mixed metal oxide coated Ti current collector. With respect to electroplating copper using an inert anode, the reaction occurring at the anode is Reaction 3.

[0042] Active and inert anodes each have their own advantages and disadvantages, as discussed herein. The primary benefit of using an active anode is that the reactions within the electroplating cell are balanced, which results in stable concentrations of metal and acid within the catholyte over time, thereby providing high quality plating results over a sustained time period. The primary benefit of using an inert anode is its long lifetime, which minimizes anode labor and material replacement costs, and the downtime associated with such replacement. These considerations are discussed further below.

[0043] As mentioned, one benefit of using an active anode is that in properly designed systems, it leads to a balanced chemical reaction within the electroplating cell. Specifically, the oxidation of the metal anode regenerates one atom of metal for each atom of metal that is consumed at the

substrate/cathode. As a result, the overall metal content within the electroplating cell is balanced, and there is no significant perturbation to the concentration of soluble species (e.g., metal, acid, etc.) during operation of the electroplating cell. In one example, the anode is an active phosphorus-doped copper anode, and every mole of Cu^{2+} consumed at the substrate is replenished with a molar equivalent of Cu^{2+} generated via oxidizing the phosphorus-doped copper anode. As such, no major adjustments need to be made to correct the concentrations of inorganic species (e.g., metal ions or protons/acid). For at least this reason, active anodes are known to considerably extend the timeframe over which a particular batch of electrolyte can be used for electroplating, as compared to inert anodes. In many cases, electrolyte used with an active anode has been known to last for 10 or more electrolyte turnovers, where each electrolyte turnover corresponds to the equivalent of the cumulative charge passed that would be required to remove the initial amount of metal dissolved within the catholyte.

[0044] More minor adjustments may be made to the catholyte and/or anolyte over time, for example to remove organic byproducts/breakdown species/contaminants in a process referred to as “bleed and feed.” These processes are particularly useful for managing the organic components within the electrolyte, and are often unnecessary for managing the inorganic components such as metal ions and acid. Eventually, the buildup of organic plating additives or photoresist residue can lead to poor plating performance and the electrolyte is removed and replaced.

[0045] FIG. 2A illustrates modeling results showing the concentration of copper and acid over time within the catholyte of an electroplating cell operating with an active anode. In this example, the modeled electroplating cell includes a cathode chamber and an anode chamber separated by a membrane, as shown in FIG. 1A. Because the reactions within the electroplating cell are balanced, the composition of the electrolyte is stable over time with respect to both copper ions and acid. This stability in electrolyte composition is highly advantageous.

[0046] One disadvantage of active anodes is that the anode itself is consumed over time, and therefore must be replaced. There are a number of factors that affect the frequency at which such replacement should be performed, including but not limited to (i) the size/mass of the anode, (ii) the time-average plating current, and (iii) the degree to which the electroplating cell is being utilized. Various geometric and ergonomic handling constraints limit the maximum anode size and weight. Operations with the highest plating currents and greatest tool utilizations require the most frequent anode replacements, and are therefore the types of operations that are most severely impacted by such replacement/maintenance events.

[0047] The process of replacing an active anode in a modern semiconductor electroplating apparatus is not trivial. These replacement processes can be invasive, cumbersome, time-

consuming, and complex, especially in the context of electroplating cells in which the anode chamber is separated from the cathode chamber as described above. In such electroplating cells, the anode itself is located below a multi-part process kit and additional hardware that is used to hermetically seal the membrane against the anode chamber. During anode replacement, the process kit, membrane, and all associated parts are first removed before cleaning out any residual anode metal and byproducts in the anode chamber. A new anode is installed before re-installing the membrane and associated sealing unit. The hermeticity of the seal is checked and tested before the remaining parts are re-installed. Often the cell must be tested and “requalified” before returning to service. In addition, the replacement process exposes maintenance personnel to possible chemical exposure, which can be dangerous. This replacement process is cumbersome and the related downtime is costly.

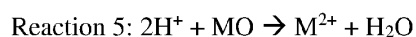
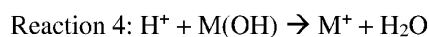
[0048] In contrast, electroplating systems that use inert anodes do not require frequent anode replacement. Inert anodes are not consumed over time and therefore do not need repeated replacement in the same manner as an active anode. In many cases, an inert anode will have a lifetime that is about 20-100x greater than the lifetime of a comparable active anode. Returning to FIG. 1B, during electroplating, the inert anode catalytically oxidizes electrolyte (e.g., the water in the electrolyte) to yield the required reducing charge equivalents according to Reaction 3, above. Water in the electrolyte is easily monitored and replaced in an automated fashion and without requiring any invasive maintenance. As shown in Reaction 3, in addition to yielding electrons, water oxidation also yields protons and dioxygen. Dioxygen dissolved gas or bubbles are easily removed from the electrolyte, for example using filtration, a high surface area contactor/degasser, and/or by letting the electrolyte vent into atmosphere.

[0049] The proton reaction products from Reaction 3 should be handled in a more comprehensive way. Otherwise, acid can accumulate in the electrolyte system. If such accumulation is left uncorrected, there is progressive (i) consumption of soluble metal species at the substrate/cathode, and (ii) generation of protons at the anode, which leads to significant concentration shifts and imbalances over time.

[0050] FIG. 2B illustrates modeling results showing the concentration of copper and acid over time within the catholyte of an electroplating cell operating with an inert anode. In this example, the modeled electroplating cell includes a cathode chamber and an anode chamber separated by a membrane, as shown in FIG. 1B. As time progresses, the catholyte loses metal cations (which are being consumed at the substrate/cathode) and is enriched in acid (which is being produced at the anode), which results in the catholyte quickly falling outside of a useful process window. In some cases, continuous removal and replacement of a portion of the catholyte (e.g., bleed and feed, as

mentioned above) can be used to sustain acceptable ion concentrations; however, the bleed and feed approach is costly, and the degree of electrolyte volume required to be removed and replaced is often impractical.

[0051] In some cases, a process known as direct metal replenishment may be used for managing ion imbalances that result from the use of inert anodes. These processes react imbalanced catholyte (e.g., one having a concentration of acid that is trending higher than desired and a concentration of metal that is trending lower than desired) with solid metal oxide powder. As an example, CuO powder is used for copper deposition, and SnO powder is used for tin deposition. The catholyte treatment used in connection with the direct metal replenishment technique is a common acid/base reaction, which consumes excess protons/acid and yields desired metal salts in the catholyte according to Reactions 4-6 and other like-kind transformations:



[0052] Direct metal replenishment can be an effective method for correcting ion imbalances in the catholyte; however, it is imperfect and limited in many respects. For example, exposing the catholyte to metal oxides or like-kind solids involves careful catholyte metrology, metering of solids/liquids into the catholyte, and appropriate timing to avoid underdosing or overdosing the catholyte. Adding too little metal oxide (or analogous material) to the catholyte can result in catholyte that is acid-rich and metal-poor (e.g., having a higher than desired acid content and a lower than desired metal content). On the other hand, adding too much metal oxide (or analogous material) to the catholyte can result in catholyte that is acid-poor and metal-rich (e.g., having a lower than desired acid content and a higher than desired metal content). Both of these cases are undesirable and can yield catholytes that fall outside of an acceptable or useful process window. Therefore, when direct metal replenishment is used to treat the catholyte, there is a need for precise and frequent dosing of the metal oxide (or analogous material) to the catholyte. Existing direct metal replenishment solutions are currently implemented using an offboard tool that performs both metrology and dosing. Those tools are expensive, and typically support only a few chemistries.

[0053] Another drawback to direct metal replenishment within the catholyte is that there is a significant risk of contaminating the catholyte. Directly exposing the catholyte to the metal oxide (or analogous material) introduces risks such as (i) particle contamination on the substrate from unreacted/insoluble metal oxide, (ii) organic contamination on the substrate if incoming solids (e.g., metal oxides) are impure, (iii) buildup of undesirable trace metal impurities from incoming metal oxides (e.g., Zn^{2+} , Fe^{3+} , oxides, sulfates, hydroxides, etc.), and (iv) breakdown of organic

plating additives as a result of reaction with the metal oxides, and unwanted introduction of contaminating byproducts that result from such reactions.

[0054] The examples herein utilize a novel approach to control the composition of electrolyte in cases where there is a membrane separating a cathode chamber from an anode chamber housing an inert anode. This approach involves exposing the anolyte to metal-replenishing and acid-reducing particles. These particles are typically provided in the form of a metal-containing material. In one example, solid particles of the metal-containing material are introduced directly into an anolyte flow loop. In another example, the particles are introduced in combination with an ion exchanger configured to improve the exposure of the anolyte to the metal replenishing chemical used to treat the anolyte. In one more example, the ion exchanger is configured as a porous solid sintered metal replenishment chemical, which may be provided as pieces or a replaceable cartridge. As the anolyte passes through the ion exchanger, it is exposed (or further exposed) to the metal-containing material. The metal-containing material is a solid that reacts with hydrogen ions in the anolyte to produce metal ions. The hydrogen ions are generated at the anode according to Reaction 3, above. The metal ions produced in the ion exchanger travel from the anode chamber, across the anode chamber membrane, and into the cathode chamber, where they are reduced at the substrate/cathode according to Reaction 1, above. The result is an electroplating cell that provides stable metal and acid concentrations while using an inert anode. In other words, the electroplating cell provides the stable electrolyte composition associated with an active anode, without the significant disadvantages associated with active anodes such as repeated anode replacement as well as the associated downtime and other costs. Likewise, the disclosed electroplating techniques avoid the costly and complex control associated with dosing the catholyte in the inert anode direct metal replenishment process, as well as the related catholyte contamination risks.

[0055] FIG. 1C presents an electroplating cell 141 having an inert anode 122 and an ion exchanger 130 as described herein. Like the examples in FIGS. 1A and 1B, the electroplating cell 141 includes a cathode chamber 106 and an anode chamber 107 separated by a membrane 105. Several types of membranes can be used to separate the catholyte and anolyte, including ultra and nanofiltration media, reverse osmosis membranes, and ionic membranes. In one example, the preferred membrane 105 is a cation exchange membrane, such as NafionTM. A cation exchange membrane allows positive ions to migrate and diffuse through them, while substantially impeding the diffusive and/or migration transport of negatively charged species (e.g., anions) and neutral compounds. A substrate 103, which acts as a cathode, is positioned in the cathode chamber 106. The inert anode 122 is positioned in the anode chamber 107.

[0056] Ion exchanger 130 is in fluidic communication with the anode chamber 107. The ion exchanger 130 includes one or more metal-containing material that reacts with hydrogen ions in the anolyte. The metal-containing material may be added to ion exchanger 130 using dosing hardware (not shown) configured to accomplish this task continuously or periodically. In some cases, the dosing hardware may be configured to add a powdered form of the metal-containing material to the anolyte. In other cases, the dosing hardware may be configured to provide the metal-containing material in a cartridge form, as described herein.

[0057] The metal-containing material should include the same type of metal that is being electroplated. In other words, if the electroplating cell 141 is being used to deposit copper, the metal-containing material in the ion exchanger 130 should be a copper-containing material. Similarly, if the electroplating cell 141 is being used to deposit tin, the metal-containing material in the ion exchanger 130 should contain tin.

[0058] If the electroplating cell 141 is being used to deposit a metal alloy including a less noble metal and a more noble metal, the metal-containing material in the ion exchanger 130 should include a material including the less noble metal. One example is discussed further below.

[0059] The metal-containing material is a heterogeneous material (e.g., including the relevant metal and at least one other element). Examples of appropriate metal-containing materials include, but are not limited to, metal oxides, metal hydroxides, metal carbonates, metal bicarbonates, and metal sulfides, etc. The metal-containing material is typically a solid, and may be provided in the form of powder, which may be fluidized, as discussed further below. In some examples, the powder may have a particular particle size. Example minimum particle sizes may include, e.g., 5um, 25um, or 100um. Example maximum particle sizes may include, e.g., 0.1mm, 1mm, or 10mm. These minimums and maximums may be combined to define ranges of particle sizes that may be used for particular examples. In some examples, the metal-containing material may have other particular properties including, e.g., porosity, surface area, density, purity, etc. In some cases the metal-containing material has anti-clumping and/or anti-caking properties.

[0060] The anolyte entering ion exchanger 130 is relatively metal-poor and acid-rich compared to the anolyte exiting the ion exchanger 130. Acid (e.g., hydrogen ions) in the anolyte reacts with the metal-containing material in the ion exchanger 130 to produce a dissolved metal salt in the treated anolyte. The metal-containing material is continuously provided at a substantial stoichiometric excess such that substantially all of the hydrogen ions in the anolyte are rapidly quenched within the anolyte recirculation loop (e.g., in this example the anolyte recirculation loop includes anode chamber 107, ion exchanger 130, and associated plumbing). As a result, the anolyte leaving the ion exchanger 130 has substantially more metal and substantially less acid

compared to the anolyte that enters the ion exchanger 130. The ion exchanger 130 essentially acts to convert excess acid (which would otherwise build up over time causing the pH of the anolyte and catholyte to drop outside of a useful process window) to plateable metal species by reacting the acid in the anolyte with the metal-containing species in the ion exchanger 130. Not only does this keep the acid at a desired concentration, it also keeps the metal ions at a desired concentration, as discussed below in connection with FIG. 2C.

[0061] As mentioned above, in certain examples the metal being electroplated is a metal alloy. One example of a commonly plated metal alloy is the solder SnAg. In cases of metal alloy plating, the anolyte contains only the less noble metal (e.g., tin), and is segregated from the catholyte containing both types of metal (e.g., tin and silver) by a membrane 105 (e.g., a cationic membrane). The more noble element (e.g., silver) is plated onto the substrate/cathode and is thereby removed from the catholyte; the catholyte is replenished of the more noble element (e.g., silver) by dosing the catholyte with a solution including ions of the more noble element (e.g., a silver ion-containing solution such as 25g/L silver methane sulphonate). The less noble metal (e.g., tin) is depleted from the catholyte as it is plated, and is replenished by the migration of ions of the less noble metal (e.g., tin) through the membrane 105 from the anode chamber 107. In order to replenish the less noble metal (e.g., tin) in the anode chamber 107, the anolyte is exposed to particle of a metal-containing material that includes the less noble metal (e.g., particles of a tin-containing material such as tin oxide). The metal-containing material reacts with acid/protons generated at the inert anode to form ions of the less noble metal (e.g., tin ions), which are then transported across the membrane 105 into the cathode chamber 106. This process is similar to the one used for plating ecobumps. The primary differences are (1) use of an inert anode, and (2) exposing the anolyte to the metal-containing material (e.g., SnO) to thereby react acid generated at the anode with the metal-containing material to produce metal ions.

[0062] Returning to the example where the metal being plated is copper, FIG. 2C depicts modeling results showing the concentration of copper and acid over time within the catholyte of an electroplating cell operating with an inert anode and an ion exchanger, as described herein. In this example, the modeled electroplating cell includes a cathode chamber and an anode chamber separated by a membrane, as shown in FIG. 1C. Much like the case with the active anode described in relation to FIG. 2A, the electrolyte does not change metal ion concentration or acid concentration over time. This stability is highly advantageous, and has not been previously achieved in the context of an electroplating apparatus having an inert anode and separated anode and cathode chambers. As such, the examples herein represent a substantial improvement in the art, achieving the electrolyte composition control typically associated with an active anode,

without the need for repeated anode replacement.

[0063] Having ion exchange occur in the anolyte, as opposed to the catholyte (e.g., as used in the direct metal replenishment strategy described above), provides substantial benefits. For instance, such a configuration ensures that the metal-containing material does not contact the substrate, where it could otherwise cause deposition of unwanted particles or other unwanted reactions. By contrast, in cases where a metal-containing material is added to the catholyte, such material may undesirably deposit directly on the substrate as unwanted particles, resulting in poor quality plating. Similarly, metal-containing material added to catholyte can interact directly with the organic plating additives and any other species present in the catholyte. Such interactions may degrade the organic plating additives, thereby causing unwanted reactions, poor plating results, and requiring more frequent replacement of the organic additives. As an example, CuO has been used to treat catholyte in direct metal replenishment strategies. The CuO typically will include not insignificant amounts of Cu₂O and other metal oxide impurities, which can react with acid in the catholyte to form cuprous ions and other reducible metal ions, which in turn react with and decompose bis(sodiumsulfopropyl)disulfide (SPS), a commonly used accelerator, or co-deposit as a metal impurity (which can impact many copper metal properties unfavorably). By contrast, when the CuO is exposed to the anolyte, as opposed to the catholyte, the membrane acts to protect the SPS from any Cu₂O impurities and the related contamination. Further, any cuprous ions present in the anolyte can react with oxygen generated at the inert anode to form stable, unreactive cupric ion and water.

[0064] Another significant benefit of treating the anolyte, as opposed to the catholyte, is that a substantial excess of metal-containing material can be used. Due to the contamination and dosing concerns described above, treating the catholyte (e.g., through direct metal replenishment) involves careful metrology and metering of the metal-containing material into the catholyte. By contrast, treating the anolyte as described herein does not require similar metrology or careful metering. Instead, the metal-containing material can be provided at a substantial excess without regard to the exact composition of the anolyte.

[0065] In certain examples, the anolyte is maintained at a low acid concentration and moderate pH (e.g., less than about 0.01 mol/L proton concentration, and a pH of about 2 or greater). Due to the high mobility of protons relative to all other ions (e.g. metal ions), protons in the anolyte are favored to move from the anolyte in the anode chamber (across the membrane under the influence of the electric field) to the cathode/catholyte in the cathode chamber. The lower the concentration of acid relative to metal in an anolyte, the greater the fractional metal ion current from the anolyte to the catholyte. It is a goal to keep this fraction close to 100%. Consider that, in an active anode

system (metal anode), acid is not generated in and removed from the anolyte over time. Though no acid is generated at the active anode, protons are favorably driven across the membrane due to the relative mobilities mentioned above, and the proton/acid concentration within the anolyte trends downward over the course of plating. In contrast, with the inert anode system, acid is formed and should be removed quickly from the system, or else the proton/acid concentration will increase and the efficiency of metal transport to the catholyte will decrease (leading to a depletion of metal and an increase in acid concentration in the catholyte). As such, in various examples herein, the anolyte is maintained at a very low acid concentration as described above. This low acid concentration can be achieved by having little acid in the anolyte at start up, and by continuously exposing the anolyte to the metal-containing material to promote ion exchange. In this way, acid generated at the anode and contained within the anode chamber is constantly exposed to and reacted with excess metal-containing material. The metal-containing material continuously and rapidly converts hydrogen ions in the anolyte recirculation loop to dissolved metal salts, such that the acid content in the anode chamber is always being driven to zero.

15 [0066] Excess metal-containing material (as well as removal of any contaminants and byproducts) can be filtered out or otherwise remove from the anolyte before the anolyte is returned to the anode chamber, as shown in connection with FIG. 3, discussed below. Further, even if there are contaminants or excess metal-containing species present in the anode chamber, the substrate, which is exposed only to the catholyte, is largely protected from the contamination due to the presence of the membrane separating the anode chamber from the cathode chamber. Generally speaking, excess metal-containing material in the anolyte is expected to be operationally easier and generally benign, as compared to having the same or similar materials in the catholyte.

25 [0067] A further benefit of treating the anolyte as opposed to the catholyte relates to increased flexibility of the metal-containing material used for such treatment, which substantially expands the types of metals that can be plated. Direct metal replenishment strategies have been developed for plating copper or tin. These strategies involve exposing the catholyte to a metal-containing material that acts as an ion exchange material. In the case of plating copper, the catholyte is exposed to CuO. In the case of plating tin, the catholyte is exposed to SnO. The products of these reactions include the desired metal salt and water as an additional benign byproduct. By contrast,

30 in the examples herein where the anolyte is treated, the choice of metal-containing material used for such treatment is less limited because the substrate is protected by the membrane from the corresponding reaction products. For instance, in an example where copper is being plated, the metal-containing material could include CuCO_3 (e.g., $2\text{H}^+ + \text{CuCO}_{3(\text{s})} \rightarrow \text{Cu}^{2+} + \text{H}^+ + \text{HCO}_3^- \rightleftharpoons \text{Cu}^{2+} + \text{H}_2\text{O} + \text{CO}_{2(\text{g})}$).

[0068] The ion exchange described herein may occur onboard or offboard the electroplating cell/apparatus. Many configurations are contemplated. Where such exchange occurs offboard, appropriate plumbing should be provided to route electrolyte to outside and back into the tool and cell, as needed.

5 [0069] FIG. 1D shows an example electroplating cell 161 similar to the one shown in FIG. 1C, and only the differences will be described. In FIG. 1C, the electroplating cell 141 includes a single membrane 105 that divides the plating chamber into a cathode chamber 106 above the membrane 105 and an anode chamber 107 below the membrane 105. By contrast, in FIG. 1D, a first membrane 105a and a second membrane 105b are provided. The first membrane 105a may be referred to as a cathode chamber membrane, and the second membrane 105b may be referred to as an anode chamber membrane. The two membranes are spaced apart from one another as shown, thereby forming middle chamber 160 above the anode chamber 107 and below the cathode chamber 106. Anolyte circulates from the anode chamber 107 into the ion exchanger 130, where it is then directed into the middle chamber 160 before being returned to the anode chamber 107, as shown. The presence of two membranes 105a and 105b, as opposed to a single membrane 105 as used in FIG. 1C, increases the resistance of acid transport to the cathode chamber. This additional resistance may be beneficial in ensuring that the acid in the catholyte remains at a desired concentration. Although the additional membrane and middle chamber are not shown in the remaining figures, it is understood that any of the examples herein may be modified to include these features.

[0070] FIGS. 1E and 1F illustrate examples of ion exchangers 130a and 130b, respectively. Details provided herein with respect to ion exchanger 130a and/or 130b may apply to any of the ion exchangers described herein, including but not limited to the ion exchanger 130 shown in FIGS. 1C and 1D, and the ion exchanger 330 shown in FIG. 3. Further, other types of hardware that are described herein as operating as ion exchangers, such as contact unit 430 and contact unit 530, as well as related metal-containing material fluidization equipment 460, may be implemented to include various features shown in ion exchangers 130a and/or 130b.

[0071] Referring to FIG. 1E, in some examples the ion exchanger 130a includes a main circulation pump 133 and one or more cartridges 131 that contain a preloaded amount of metal-containing material therein (e.g., CuO for plating copper). The cartridge 131 includes an inlet configured to receive anolyte, an outlet configured to deliver anolyte, an internal fluid path connecting the inlet to the outlet, and the metal-containing material. As anolyte passes through the internal fluid path, it is exposed to the metal-containing material. As such, the cartridge 131 acts as dosing hardware.

[0072] The composition of the anolyte entering the cartridge 131 is relatively high in acid (H^+ ions) and low in metal ions. The acid reacts with the metal-containing material in the cartridge 131 to generate metal ions. As such, the anolyte leaving the cartridge 131 has a lower acid content and a higher metal content compared to the anolyte entering the cartridge 131.

5 [0073] In one example (not shown), the cartridge 131 internally contains a fine-sized filter media (e.g., having filter size of about 0.05 μm), which may be placed in the cartridge 131 after fluid contacts the metal-containing material. This filter media may act to maintain the metal-containing material within the cartridge 131, even including fine particles. The filter media size should be
10 small enough to retain the particles of metal-containing material even as they are consumed and shrink.

[0074] This cartridge approach is relatively simple in principle, but can be difficult to implement effectively. Unfortunately, many of the metal source materials available (e.g., the metal-containing materials used herein) either (1) exhibit an extremely high resistance to flow, or (2) can
15 change when exposed to the electrolyte, thereby increasing their resistance to flow. In either case, flowing an appreciable amount of fluid through the loaded cartridge can be extremely difficult. While not wanting to be held to any model or theory, it is believed that the increase in flow resistance occurs because of two phenomena: (1) viscous forces press on the small particles of metal-containing material, causing them to progressively pack more tightly, and (2) the particles
20 undergo a size, surface and volumetric modification due to an Ostwald ripening process.

[0075] Therefore, in various examples such as the one shown in FIG. 1E, a high-pressure pump 132 (e.g., a high pressure gear pump) is used to force fluid through the metal-containing material in the cartridge 131. As mentioned above, in various examples main circulation pump 133, which may be a relatively higher flow rate/lower pressure capable pump compared to high-pressure pump
25 132, is used to recirculate the majority (e.g., 80%) of the fluid from the anode chamber and through an (optional) filter 134, while a portion of the total flow into the ion exchanger 130a is diverted via a line T to enter high-pressure pump 132 to be exposed to the metal-containing material inside the cartridge 131.

[0076] In some examples, the cartridge 131 contains one or more internal metal oxide solid
30 pellets or puck-shaped elements having a porosity between about 20% and about 60%. These pellets or pucks can be manufactured by sintering powder at an elevated temperature to form solid objects. The internal flow within the cartridge 131 is designed to uniformly expose the various surfaces of one or more metal replenishment elements (e.g., the metal-containing material in the form of pellets, puck-shaped elements, etc.) to the incoming electrolyte, uniformly flowing the

fluid to and through the elements, before returning the reacted material (e.g., the metal-rich anolyte) to the outlet of the cartridge 131. The design of the inlet and exhaust flow paths within the cartridge 131, and the porosity and the particle sizes of the metal-containing material in the metal replenishment elements can be optimized for uniform exposure of electrolyte to the reactive material. The cartridge 131 can be isolated by an inlet valve 135 and outlet valve 136 to allow circulation to continue during a cartridge 131 replacement.

[0077] Additionally, with a pair of three-way valves 135 and 136 (or equivalently a pair of two two-way valves), the cartridge 131 can be flushed with solvent such as DI water. The solvent enters the ion exchanger 130a through inlet 137, then passes through three-way valve 135 and high-pressure pump 132 before entering cartridge 131. After flushing through cartridge 131, the solvent passes through three-way valve 136 before exiting the ion exchanger 130a at rinse waste outlet 138. The cartridge 131 can have quick disconnect fittings to facilitate the unit's removal and replacement.

[0078] Referring to FIG. 1F, two or more cartridges 131a and 131b can be arranged in an isolatable parallel fashion. This parallel configuration may be used to increase the capacity of the ion exchanger, and/or to enable uninterrupted, continuous operation in the case that one of the cartridges 131a or 131b is replaced or otherwise taken out of service. In this way, there is always at least one cartridge 131a or 131b that is available to react with the anolyte, as needed. In various examples where multiple cartridges are provided in the ion exchanger (e.g., such as the example shown in FIG. 1F), each cartridge may have its own high-pressure pump, inlet control valves, and outlet control valves. For instance, cartridge 131a has a dedicated high-pressure pump 132a, inlet valve 135a, and outlet valve 136a, while cartridge 131b has high-pressure pump 132b, inlet valve 135b, and outlet valve 136b. This parallel configuration allows each cartridge 131a and 131b to be separately rinsed with DI water or other solvents prior to removal of either cartridge 131a or 131b.

[0079] While many of the examples herein introduce the metal-containing material to the anolyte at a particular location that is remote from the anode chamber (e.g., at some point in the anolyte recirculation loop other than the anode chamber), it is understood that this is done for the sake of convenience, and that the metal-containing material may be added to the anolyte recirculation loop at any point, including directly to the anode chamber. While there are certain advantages to adding the metal-containing material at locations remote from the anode chamber, the primary goal of the examples herein (e.g., exposing the anolyte to metal-containing material to thereby react the metal-containing material with hydrogen ions generated at the inert anode to produce dissolved metal ions) can be accomplished regardless of where the anolyte is exposed to

the metal-containing material.

[0080] FIG. 3 presents an electroplating system 300 according to an example herein. Electroplating cell 301 includes cathode chamber 306 and anode chamber 307, separated by membrane 305. Membrane 305 is an ion exchange membrane such as NafionTM. A substrate 303 is positioned in the cathode chamber 306, and an inert anode 322 is positioned in the anode chamber 307.

[0081] An ion exchanger 330 is in fluidic communication with the anode chamber 307. Ion exchanger 330 is analogous to ion exchanger 130 of FIGS. 1C and 1D, as well as ion exchanger 130a of FIG. 1E and ion exchanger 130b of FIG. 1F, and any details provided above in relation to ion exchangers 130, 130a, or 130b may also apply to ion exchanger 330. Briefly, ion exchanger 330 includes a heterogeneous metal-containing material that includes the type of metal being electroplated. The metal-containing material may be added to ion exchanger 330 using dosing hardware (not shown) configured to accomplish this task continuously or periodically. In some cases, the dosing hardware may be configured to add a powdered form of the metal-containing material to the anolyte. In other cases, the dosing hardware may be configured to provide the metal-containing material in a cartridge form, as described herein.

[0082] Anolyte passes from the anode chamber 307, through pump 331, through the ion exchanger 330, and then through filter 332 before returning to the anode chamber 307. In some cases, filter 332 may be omitted. In certain examples, the metal-containing material may be supplied to the ion exchanger 330 as a porous sintered powder element, and the ion exchanger 330 may be designed so that anolyte can come in contact with and/or pass through the pores of the metal containing material. As the anolyte is exposed to the metal-containing material, acid in the anolyte reacts with the metal-containing material to form dissolved metal ions/dissolved metal salts. In another example the metal-containing material of the ion exchanger 330 is retained within one or more ion exchange cartridge retaining a porous filter media. The cartridge allows the metal-containing material to be retained within the ion exchange cartridge while anolyte passes over and/or through the ion exchange cartridge, thereby allowing acid in the anolyte to react with the metal-containing material in the ion exchange cartridge to form dissolved metal ions/dissolved metal salts.

[0083] Anolyte entering ion exchanger 330 is relatively acid-rich and metal-poor. As the anolyte passes through the ion exchanger 330, excess acid/hydrogen ions react with the metal-containing material in the ion exchanger 330 to produce desired metal salts, which are dissolved in the anolyte. The anolyte leaving ion exchanger 330 is therefore relatively acid-poor and metal-rich, as compared to the anolyte that enters ion exchanger 330.

[0084] In some examples, the filter 332 and/or the pump 331 may be part of the ion exchanger 330. In other examples, these elements are distinct and may be positioned upstream/downstream from one another. Together, the anode chamber 307, pump 331, ion exchanger 330, filter 332, and the associated plumbing form an anolyte recirculation loop. Similarly, a catholyte recirculation loop is formed by the cathode chamber 306, pump 341, and catholyte reservoir 342. While the catholyte recirculation loop is not a critical aspect of the examples herein, such loops may be implemented in any such examples to promote the highest quality plating results.

[0085] Returning to FIG. 3, filter 332 may be configured to trap any particles present in the anolyte leaving the ion exchanger 330. Such particles are typically the metal-containing materials used in the ion exchanger, but may also be non-reactive materials, byproducts, contaminants, etc. In this way, particles in the anolyte can be prevented from entering the anode chamber 307, where they could otherwise react with or on the inert anode 322 or membrane 305 in an undesirable manner. While the membrane 305 serves as a particle barrier, such particles are further prevented from entering the cathode chamber 306 when filter 332 is present. This result is highly desirable because these particles could otherwise deposit on the substrate, react with organic plating additives, or cause other issues if they reach cathode chamber 306.

[0086] In some cases, it may be desirable for several electroplating cells or several electroplating apparatuses to share a common ion exchanger and/or related hardware (e.g., filters, pumps, etc.). Also, it may be desirable to enable the metal-containing material to be fed and replenished to the anolyte in a continuous manner (e.g., by adding a powdered or solution form of the metal-containing material to the anolyte over time) instead of a batch manner that relies on cartridge replacement, thereby allowing for uninterrupted operation. FIG. 4 presents a view of an electroplating system 400 having a single electroplating apparatus 401 having two electroplating cells therein. In this example, each electroplating cell includes a cathode chamber 406 and an anode chamber 407, separated by a membrane (not labeled). The electroplating cells share a catholyte reservoir 442, a catholyte flow pump (not labeled), an anolyte reservoir 450, and an anolyte pump (not labeled). During plating, catholyte circulates through the catholyte recirculation loops, each of which includes one of the cathode chambers 406, the catholyte reservoir 442, and associated plumbing. Similarly, anolyte circulates through the anolyte recirculation loops, each of which includes one of the anode chambers 407, the anolyte reservoir 450, and additional elements as shown in FIG. 4.

[0087] Anolyte leaving the anolyte reservoir 450 can be routed to an anolyte contacting unit referred to herein as contact unit 430 and/or to metal-containing material fluidization equipment 460. The metal-containing material fluidization equipment 460 serves the purpose of providing

the metal-containing material 457 to the anolyte. In a specific example, the metal-containing material is a metal oxide powder (e.g., CuO powder in the context of plating copper). Generally speaking, the metal-containing material fluidization equipment 460 includes (i) a mixing tank 440 for holding anolyte having the metal-containing material suspended in a fluidized form therein, 5 (ii) dosing/delivery hardware (not shown) for introducing and maintaining controlled amounts of the metal-containing material 457 to the anolyte residing in the mixing tank 440, and (iii) mixing hardware 456 (e.g., an impeller or other type of mixing hardware) for suspending the metal-containing material 457 within the anolyte in the mixing tank 440.

[0088] The dosing hardware can be configured in a variety of ways, however, various examples 10 will invoke i) a storage or bulk feed system for accessing a reservoir of the metal-containing material, ii) a mechanism for measuring aliquots of the metal-containing material, and iii) a dispensing system for delivering the measured aliquot to the mixing tank 440 or anolyte. The storage, measurement, and dispensing systems can be imagined as separated hardware components or as having multipurpose functions (e.g., measure and dispense functions executed by a single 15 part like an auger, scoop, or otherwise). The dosing hardware can be configured as either a feed-forward or a feed-back system that is well-integrated with the upstream reservoir of bulk metal-containing material, the mixing tank 440, and/or the electroplating modules.

[0089] In some cases, the dosing hardware is relatively simple, and need not include all of these elements. For example, as explained in relation to FIGS. 1E-1F, the dosing hardware can be 20 implemented as one or more cartridge (e.g., cartridge 131, 131a, 131b) configured to expose the anolyte flowing therethrough to the metal-containing material. Generally speaking, any hardware used to expose the anolyte to the metal-containing material may be considered dosing hardware, as used herein.

[0090] Many configurations and types of hardware can be used to dose and fluidize, mix, and 25 create a suspension of the metal-containing material 457 into the anolyte, as desired.

[0091] In this example, the anolyte can be delivered to mixing tank 440, where metal-containing material 457 is added to the anolyte. Mixing hardware 456 may be used to suspend the metal-containing material within the anolyte. The mixing tank 440 may include a level sensor 455 that senses the level of fluid within the mixing tank 440. Output from the level sensor 455 may be 30 used to control the flow of anolyte and/or metal-containing material 457 into the mixing tank 440, thereby ensuring that the anolyte within the mixing tank remains at a desired volume and composition. Further, the fluid properties (e.g., pH, density, conductivity, temperature, etc.) of the anolyte may be measured/monitored with additional sensors (not shown) within the mixing tank 440, within the anolyte reservoir 450, and/or in the associated plumbing, and such measurements

may be used in connection with automated control processes.

[0092] As shown in FIG. 4, anolyte may be routed through an optional contact unit 430 before returning to the anode chambers 407. Contact unit 430 may be at least partly analogous to filter 332 in FIG. 3, and details provided with regard to filter 332 may also apply to contact unit 430. In a specific example, contact unit 430 includes a particle retaining filter media, which may be provided in the form of a cartridge. Generally, contact unit 430 acts to (i) expose the recirculating anolyte to the metal-containing material, and (ii) filter out the metal-containing material and other particles present in the anolyte before the anolyte is routed back to the anode chambers 407. At a basic level, both the metal-containing material fluidization equipment 460 and the contact unit 430 operate as ion exchangers, as described herein. For instance, during operation metal-containing material is present within the mixing tank 440 and within the contact unit 430. As such, anolyte can become relatively more acid-poor and metal-rich by passing through either or both of these pieces of hardware.

[0093] In some examples, contact unit 430 may be a filter cartridge having a filter size smaller than the suspended particles. In some examples, contact unit 430 may be a recirculating cyclone that separates the metal-containing material particles from the bulk anolyte stream by relying on a difference in density. Other filtration methods such as filtration bags or stilling tanks, and combinations of such methods, can also be used.

[0094] In some examples, valves 461 and 462 may be configured to ensure that anolyte is actively flowing from the electroplating apparatus 401 to the metal-containing material fluidization equipment 460, and vice versa, during electroplating. In other examples, these valves 461 and 462 may be configured to ensure that anolyte only flows between the electroplating apparatus 401 and the metal-containing material fluidization equipment 460 at select times such as when no substrate is actively being plated. A combination of these approaches may also be used. For example, electrolyte can continuously flow between the anode chambers 407, anolyte reservoir 450, pump and contact unit 430, but periodically, valve 462 can open to allow suspended metal-containing material to flow into and replenish the contact unit 430, thereby also increasing the total fluid volume in the anolyte loop, including anolyte reservoir 450. As a result of that replenishment process, the fluid level in the fluidization equipment 460 and associated mixing tank 440 will decrease. Therefore, at the same time, or at some other time, the way valve 461 can be opened to direct anolyte from the anolyte reservoir 450 to the mixing tank 440. This set of operations keeps the fluid levels in anolyte reservoir 450 and mixing tank 440 within desired operating ranges (e.g., this fluid balancing prevents all relevant hardware from running dry or overflowing). The transfer of anolyte to mixing tank 440 will dilute the concentration of metal-

containing material in the mixing tank 440, and so, at that time or some other time periodically, metal-containing material 457 is added to mixing tank 440 in a controlled amount to replenish the available metal-containing material and re-concentrate the circulating suspension. Generally speaking, valves 461 and 462 may be operated to ensure that there is always a substantial excess of metal-containing material present in the contact unit 430, such that substantially all of the hydrogen ions that enter contact unit 430 react with the metal-containing material to produce dissolved metal salts.

[0095] In some examples, a differential pressure sensor (not shown) may be implemented to measure the differential pressure of the anolyte upstream vs. downstream from contact unit 430.

The measured differential pressure can be used to determine the amount of metal containing material held in the unit, and control the position of valves 461 and 462 to ensure that there is a constant supply of new metal-containing material into the anolyte, as needed. Similarly, one or more additional sensors (e.g., pH, density, conductivity, optical absorption etc.) may be optionally provided to measure one or more properties of the anolyte downstream from contact unit 430.

[0096] FIG. 5 presents another example electroplating system 500 where metal-containing material fluidization equipment 460 is provided along with an electroplating apparatus 501 having multiple electroplating cells. The example of FIG. 5 shares many similarities with the example of FIG. 4, and only the differences will be mentioned. In the example of FIG. 5, each electroplating cell is equipped with its own anolyte reservoir 550 (as opposed to the shared anolyte reservoir 450 of FIG. 4), and its own contact unit 530 (as opposed to the shared contact unit 430 of FIG. 4). The metal-containing material fluidization equipment 460 supplies the suspended metal-containing material to an internal trunk line 565 on the electroplating apparatus 501. The internal trunk line can support processing for several plating cells equipped with anode chambers 407 and related anode recirculation loops, each having a contact unit 530. Each anolyte recirculation loop (e.g., each feeding a different electroplating cell) can be fed with its own valve trigger line to increase the amount of suspension held within each contact unit 530. A flow resistor 566 may be provided as shown to support adequate head pressure for the recirculating pump and direct the metal-containing material suspension when the appropriate valves are opened.

[0097] FIG. 6 presents an example electroplating system 600 where metal-containing material fluidization equipment 460 is shared among several distinct electroplating apparatuses 601. This example shares many similarities with the examples shown in FIGS. 4 and 5, and only the differences will be highlighted. In the example of FIG. 6, the metal-containing material fluidization equipment 460 is a central piece of equipment supporting many plating tools and supplies a recirculating line of suspended metal-containing material. In this example, the metal-

containing material fluidization equipment 460 may be located and maintained, for example, in a semiconductor fabrication facility known colloquially as a “sub-fab,” which may be physically remote and/or separated from one or more clean rooms in which the electroplating apparatuses 601 are located. Slurry from the recirculating line is directed in and out of several electroplating apparatuses 601, each of which includes one or more anolyte loops having (i) an anolyte reservoir (not shown, analogous to anolyte reservoir 450 of FIG. 4 or anolyte reservoir 550 of FIG. 5), and (ii) a contact unit (not shown, analogous to contact unit 430 of FIG. 4 or contact unit 530 of FIG. 5).

[0098] Because the metal-containing fluidization equipment can be implemented outside of the electroplating apparatus, it is very easy to add the metal-containing material to the electrolyte as needed. By contrast, when an active anode has been sufficiently consumed and needs replacement, the tool must be opened and a complex anode replacement procedure must be performed. Avoiding this replacement procedure is advantageous.

[0099] Several configurations are contemplated for implementing the metal-containing fluidization equipment. In some cases, the metal-containing fluidization equipment may be part of an electroplating apparatus, or may be housed in the same room as the electroplating apparatus without any special considerations. In various other cases, the metal-containing fluidization equipment may be implemented at a location that is physically separated (e.g., by distance and/or barriers) from the electroplating apparatus. In many cases, the electroplating apparatus operates in a clean room to promote high quality plating results. Clean room standards may not allow the introduction of the metal-containing material within the clean room itself, for example because the metal-containing material is typically provided in the form of a powder, which can be difficult to control. As such, the metal-containing material fluidization equipment may be located outside of a clean room housing the electroplating apparatus. In many cases, the metal-containing material fluidization equipment can be located in facilities that are relatively less sensitive to particle contamination issues. These areas are often referred to as the “sub-fab.” Plumbing may be provided to route the anolyte as desired. For instance, one or more pressurized slurry supply lines may be provided to pump anolyte having the metal-containing material suspended therein from the metal-containing material fluidization equipment to the electroplating apparatuses. In this way, various electroplating apparatuses can feed from the pressurized slurry supply line, as illustrated in FIG. 6.

[0100] In another example, the metal-containing material fluidization equipment may be provided within the clean room housing the electroplating apparatus(es). A sub-environment is provided within the clean room, and the metal-containing powder fluidization equipment is

positioned within this sub-environment. The sub-environment can be equipped with a HEPA filter to ensure that no airborne particles such as powder escapes from the sub-environment into the rest of the clean room. Plumbing may be provided to route the anolyte as desired between the sub-environment and the electroplating apparatus(es). Pre-packaged, clean room-compatible bags or other containers of metal-containing material can be brought into the sub-environment, and automated handling equipment can be used to open the bags/containers after the sub-environment is closed, without risk of exposing the clean room to the metal-containing material. These approaches can also be combined.

[0101] The examples herein provide a novel approach to controlling electrolyte composition.

The proposed strategies represent a significant advancement over existing, catholyte-based control methods such as direct metal replenishment for many reasons, as described throughout this document. Briefly, the disclosed approach is far simpler and more cost effective to implement because it does not require careful metrology or metering of reagents (e.g., metal-containing material) into the catholyte. Rather, the anolyte is exposed to an excess of the metal-containing material at some point in the anolyte recirculation loop, such that acid generated at the inert anode is rapidly quenched and dissolved metal salts are produced from the metal-containing material. In addition to simplifying the control scheme, addition of the metal-containing material to the anolyte protects the catholyte and substrate from a host of contamination-related concerns including unwanted reactions, formation and deposition of particles, breakdown of organic plating additives, etc. Combined, these advantages offer significant advancement over existing technologies, and enable long-term implementation of inert anode implementations for various chemistries and plating configurations.

[0102] The techniques described herein may be performed on any appropriate apparatus. FIG. 7 presents an example of an electroplating cell in which electroplating may occur. Any of the electroplating apparatus and systems described herein may have one or more electroplating cell as shown and described in relation to FIG. 7. Often, an electroplating apparatus includes one or more electroplating cells in which the substrates (e.g., wafers) are processed. Only one electroplating cell is shown in FIG. 7 to preserve clarity. To optimize bottom-up electroplating, additives (e.g., accelerators, suppressors, and levelers) are added to the electrolyte; however, an electrolyte with additives may react with the anode in undesirable ways, as described above. Therefore anodic and cathodic regions of the plating cell are often separated by a membrane so that plating solutions of different composition may be used in each region, as described herein. A number of engineering designs can be used in order to introduce anolyte and catholyte into the plating apparatus.

[0103] Referring to FIG. 7, a diagrammatical cross-sectional view of an electroplating apparatus

701 in accordance with one example is shown. The plating bath 703 contains the plating solution, also referred to as the electrolyte, which is shown at a level 705. The catholyte portion of this vessel, also referred to as the cathode chamber, is adapted for receiving substrates in a catholyte. A wafer 707 is immersed into the plating solution and is held by, e.g., a “clamshell” substrate holder 709, mounted on a rotatable spindle 711, which allows rotation of clamshell substrate holder 709 together with the wafer 707.

[0104] An anode 713 is disposed below the wafer within the plating bath 703 and is separated from the wafer region by a membrane 715, preferably an ion selective membrane. For example, Nafion™ cationic exchange membrane (CEM) may be used. The region below the anodic membrane is often referred to as an anode chamber. The membrane 715 is ion-selective and allows ionic communication between the anodic and cathodic regions of the plating cell, while preventing the particles generated at the anode from entering the proximity of the wafer and contaminating it. The membrane is also useful in redistributing current flow during the plating process and thereby improving the plating uniformity. Ion exchange membranes, such as cationic exchange membranes, are especially suitable for these applications. These membranes are typically made of ionomeric materials, such as perfluorinated co-polymers containing sulfonic groups (e.g. Nafion™), sulfonated polyimides, and other materials known to those of skill in the art to be suitable for cation exchange. Selected examples of suitable Nafion™ membranes include N324 and N424 membranes available from Dupont de Nemours Co.

[0105] During plating the ions from the plating solution are deposited on the substrate. The metal ions must diffuse through the diffusion boundary layer and into the TSV hole or other feature. A typical way to assist the diffusion is through convection flow of the electroplating solution provided by the pump 717. Additionally, a vibration agitation or sonic agitation member may be used as well as wafer rotation. For example, a vibration transducer 708 may be attached to the clamshell substrate holder 709.

[0106] The plating solution is continuously provided to plating bath 703 by the pump 717. Generally, the plating solution flows upwards through an membrane 715 and a diffuser plate 719 to the center of wafer 707 and then radially outward and across wafer 707. The plating solution also may be provided into the anodic region of the bath from the side of the plating bath 703. The plating solution then overflows plating bath 703 to an overflow reservoir 721. The plating solution is then filtered (not shown) and returned to pump 717 completing the recirculation of the plating solution. In certain configurations of the plating cell, a distinct electrolyte is circulated through the portion of the plating cell in which the anode is contained while mixing with the main plating solution is prevented using sparingly permeable membranes or ion selective membranes.

[0107] A reference electrode 731 is located on the outside of the plating bath 703 in a separate chamber 733, which chamber is replenished by overflow from the plating bath 703. Alternatively, in some examples the reference electrode is positioned as close to the substrate surface as possible, and the reference electrode chamber is connected via a capillary tube or by another method, to the side of the wafer substrate or directly under the wafer substrate. In some of the preferred examples, the apparatus further includes contact sense leads that connect to the wafer periphery and which are configured to sense the potential of the metal seed layer at the periphery of the wafer but do not carry any current to the wafer.

[0108] A reference electrode 731 is typically employed when electroplating at a controlled potential is desired. The reference electrode 731 may be one of a variety of commonly used types such as mercury/mercury sulfate, silver chloride, saturated calomel, or copper metal. A contact sense lead in direct contact with the wafer 707 may be used in some examples, in addition to the reference electrode, for more accurate potential measurement (not shown).

[0109] A power supply 735 (e.g., DC power supply) can be used to control current flow to the wafer 707. The power supply 735 has a negative output lead 739 electrically connected to wafer 707 through one or more slip rings, brushes and contacts (not shown). The positive output lead 741 of power supply 735 is electrically connected to an anode 713 located in plating bath 703. The power supply 735, a reference electrode 731, and a contact sense lead (not shown) can be connected to a system controller 747, which allows, among other functions, modulation of current and potential provided to the elements of electroplating cell. For example, the controller may allow electroplating in potential-controlled and current-controlled regimes. The controller may include program instructions specifying current and voltage levels that need to be applied to various elements of the plating cell, as well as times at which these levels need to be changed. When forward current is applied, the power supply 735 biases the wafer 707 to have a negative potential relative to anode 713. This causes an electrical current to flow from anode 713 to the wafer 707, and an electrochemical reduction (e.g. $\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}^0$) occurs on the wafer surface (the cathode), which results in the deposition of the electrically conductive layer (e.g. copper) on the surfaces of the wafer. An inert anode 714 may be installed below the wafer 707 within the plating bath 703 and separated from the wafer region by the membrane 715.

[0110] The apparatus may also include a heater 745 for maintaining the temperature of the plating solution at a specific level. The plating solution may be used to transfer the heat to the other elements of the plating bath. For example, when a wafer 707 is loaded into the plating bath the heater 745 and the pump 717 may be turned on to circulate the plating solution through the electroplating apparatus 701, until the temperature throughout the apparatus becomes substantially

uniform. In one example the heater is connected to the system controller 747. The system controller 747 may be connected to a thermocouple to receive feedback of the plating solution temperature within the electroplating apparatus and determine the need for additional heating.

[0111] The controller will typically include one or more memory devices and one or more processors. The processor may include a CPU or computer, analog and/or digital input/output connections, stepper motor controller boards, etc. In certain examples, the controller controls all of the activities of the electroplating apparatus. Non-transitory machine-readable media containing instructions for controlling process operations in accordance with the present examples may be coupled to the system controller.

[0112] Typically there will be a user interface associated with system controller 747. The user interface may include a display screen, graphical software displays of the apparatus and/or process conditions, and user input devices such as pointing devices, keyboards, touch screens, microphones, etc. The computer program code for controlling electroplating processes can be written in any conventional computer readable programming language: for example, assembly language, C, C++, Pascal, Fortran or others. Compiled object code or script is executed by the processor to perform the tasks identified in the program. One example of a plating apparatus that may be used according to the examples herein is the Lam Research Sabre tool. Electrodeposition can be performed in components that form a larger electrodeposition apparatus.

[0113] Although not shown in FIG. 7, it is understood that the electroplating apparatus 701 may be adapted to include one or more anolyte recirculation loop as described herein. For instance, the anolyte recirculation loop may include one or more ion exchanger, which may be implemented as one or more mixing tank and/or one or more contact units, for example as described in relation to FIG. 1C and FIGS. 3-6.

[0114] An alternative example of an electrodeposition apparatus 800 is schematically illustrated in FIG. 8. Again, while not shown in FIG. 8, it is understood that the apparatus may be adapted to include one or more anolyte recirculation loop as described herein. In the example of FIG. 8, the electrodeposition apparatus 800 has a set of electroplating cells 807, each containing an electroplating bath, in a paired or multiple “duet” configuration. In addition to electroplating *per se*, the electrodeposition apparatus 800 may perform a variety of other electroplating related processes and sub-steps, such as spin-rinsing, spin-drying, metal and silicon wet etching, electroless deposition, pre-wetting and pre-chemical treating, reducing, annealing, electro-etching and/or electropolishing, photoresist stripping, and surface pre-activation, for example. The electrodeposition apparatus 800 is shown schematically looking top down in FIG. 8, and only a single level or “floor” is revealed in the figure, but it is to be readily understood by one having

ordinary skill in the art that such an apparatus, e.g., the Lam Sabre™ 3D tool, can have two or more levels “stacked” on top of each other, each potentially having identical or different types of processing stations.

[0115] Referring once again to FIG. 8, the substrates 806 that are to be electroplated are generally fed to the electrodeposition apparatus 800 through a front end loading FOUP 801 and, in this example, are brought from the FOUP to the main substrate processing area of the electrodeposition apparatus 800 via a front-end robot 802 that can retract and move a substrate 806 driven by a spindle 803 in multiple dimensions from one station to another of the accessible stations—two front-end accessible stations 804 and also two front-end accessible stations 808 are shown in this example. The front-end accessible stations 804 and 808 may include, for example, pre-treatment stations, and spin rinse drying (SRD) stations. Lateral movement from side-to-side of the front-end robot 802 is accomplished utilizing robot track 802a. Each of the substrates 806 may be held by a cup/cone assembly (not shown) driven by a spindle 803 connected to a motor (not shown), and the motor may be attached to a mounting bracket 809. Also shown in this example are the four “duets” of electroplating cells 807, for a total of eight electroplating cells 807. A system controller (not shown) may be coupled to the electrodeposition apparatus 800 to control some or all of the properties of the electrodeposition apparatus 800. The system controller may be programmed or otherwise configured to execute instructions according to processes described earlier herein.

20

System Controller

[0116] In some implementations, a controller is part of a system, which may be part of the above-described examples. Such systems can comprise semiconductor processing equipment, including a processing tool or tools, chamber or chambers, a platform or platforms for processing, and/or specific processing components (a wafer pedestal, a gas flow system, etc.). These systems may be integrated with electronics for controlling their operation before, during, and after processing of a semiconductor wafer or substrate. The electronics may be referred to as the “controller,” which may control various components or subparts of the system or systems. The controller, depending on the processing requirements and/or the type of system, may be programmed to control any of the processes disclosed herein, including the delivery of processing gases, temperature settings (e.g., heating and/or cooling), pressure settings, vacuum settings, power settings, radio frequency (RF) generator settings, RF matching circuit settings, frequency settings, flow rate settings, fluid delivery settings, positional and operation settings, wafer transfers into and out of a tool and other transfer tools and/or load locks connected to or interfaced with a specific

30

system.

[0117] Broadly speaking, the controller may be defined as electronics having various integrated circuits, logic, memory, and/or software that receive instructions, issue instructions, control operation, enable cleaning operations, enable endpoint measurements, and the like. The integrated
5 circuits may include chips in the form of firmware that store program instructions, digital signal processors (DSPs), chips defined as application specific integrated circuits (ASICs), and/or one or more microprocessors, or microcontrollers that execute program instructions (e.g., software). Program instructions may be instructions communicated to the controller in the form of various individual settings (or program files), defining operational parameters for carrying out a particular
10 process on or for a semiconductor wafer or to a system. The operational parameters may, in some examples, be part of a recipe defined by process engineers to accomplish one or more processing steps during the fabrication of one or more layers, materials, metals, oxides, silicon, silicon dioxide, surfaces, circuits, and/or dies of a wafer.

[0118] The controller, in some implementations, may be a part of or coupled to a computer that
15 is integrated with, coupled to the system, otherwise networked to the system, or a combination thereof. For example, the controller may be in the “cloud” or all or a part of a fab host computer system, which can allow for remote access of the wafer processing. The computer may enable remote access to the system to monitor current progress of fabrication operations, examine a history of past fabrication operations, examine trends or performance metrics from a plurality of
20 fabrication operations, to change parameters of current processing, to set processing steps to follow a current processing, or to start a new process. In some examples, a remote computer (e.g. a server) can provide process recipes to a system over a network, which may include a local network or the Internet. The remote computer may include a user interface that enables entry or programming of parameters and/or settings, which are then communicated to the system from the remote computer.
25 In some examples, the controller receives instructions in the form of data, which specify parameters for each of the processing steps to be performed during one or more operations. It should be understood that the parameters may be specific to the type of process to be performed and the type of tool that the controller is configured to interface with or control. Thus as described above, the controller may be distributed, such as by comprising one or more discrete controllers
30 that are networked together and working towards a common purpose, such as the processes and controls described herein. An example of a distributed controller for such purposes would be one or more integrated circuits on a chamber in communication with one or more integrated circuits located remotely (such as at the platform level or as part of a remote computer) that combine to control a process on the chamber.

[0119] Without limitation, example systems may include a plasma etch chamber or module, a deposition chamber or module, a spin-rinse chamber or module, a metal plating chamber or module, a clean chamber or module, a bevel edge etch chamber or module, a physical vapor deposition (PVD) chamber or module, a chemical vapor deposition (CVD) chamber or module, an atomic layer deposition (ALD) chamber or module, an atomic layer etch (ALE) chamber or module, an ion implantation chamber or module, a track chamber or module, and any other semiconductor processing systems that may be associated or used in the fabrication and/or manufacturing of semiconductor wafers.

[0120] As noted above, depending on the process step or steps to be performed by the tool, the controller might communicate with one or more of other tool circuits or modules, other tool components, cluster tools, other tool interfaces, adjacent tools, neighboring tools, tools located throughout a factory, a main computer, another controller, or tools used in material transport that bring containers of wafers to and from tool locations and/or load ports in a semiconductor manufacturing factory.

CONCLUSION

[0121] Although the foregoing examples have been described in some detail for purposes of clarity of understanding, it will be apparent that certain changes and modifications may be practiced within the scope of the appended claims. It should be noted that there are many alternative ways of implementing the processes, systems, and apparatus of the present examples. Accordingly, the present examples are to be considered as illustrative and not restrictive, and the examples are not to be limited to the details given herein.

CLAIMS

What is claimed is:

1. A system for electroplating a metal on a substrate, the system comprising:
 - 5 an electroplating cell comprising:
 - an anode, wherein the anode is an inert anode,
 - a cathode chamber configured to hold catholyte and receive the substrate during electroplating such that the substrate is exposed to the catholyte,
 - an anode chamber configured to hold anolyte and the anode during electroplating,
 - 10 a membrane configured to separate the cathode chamber from the anode chamber, wherein the membrane permits passage of ions from the anode chamber to the cathode chamber during electroplating and prevents passage of organic compounds from the cathode chamber to the anode chamber during electroplating; and
 - dosing hardware configured to provide a metal-containing material to the anolyte, wherein the
 - 15 metal-containing material is a heterogeneous material comprising the metal being electroplated on the substrate.
 2. The system of claim 1, wherein the metal-containing material comprises at least one of a metal oxide, a metal hydroxide, a metal carbonate, a metal bicarbonate, or a metal sulfide.
 3. The system of claim 1, further comprising a filter, wherein the filter is configured to
 - 20 remove the metal-containing material from the anolyte.
 4. The system of claim 1, wherein the dosing hardware comprises a mixing tank in fluidic communication with the anode chamber and a mixer for fluidizing the metal-containing material within the mixing tank.
 5. The system of claim 4, further comprising a trunk line configured to deliver a slurry
 - 25 comprising the anolyte and the metal-containing material from the mixing tank toward the anode chamber.

6. The system of claim 5, comprising a plurality of distinct electroplating apparatuses, each having at least one electroplating cell, wherein the trunk line is configured to deliver the slurry to the plurality of distinct electroplating apparatuses.
7. The system of claim 4, wherein the electroplating cell is positioned in a clean room of a semiconductor fabrication facility, and wherein the mixing tank is positioned either (i) outside of the clean room of the semiconductor fabrication facility, or (ii) within a sub-environment within the clean room of the semiconductor fabrication facility, wherein the sub-environment comprises a filter that enables use of powdered material within the sub-environment without contaminating the rest of the clean room.
8. The system of claim 1, further comprising a controller configured to cause introduction of the metal-containing material to the anolyte.
9. The system of claim 8, further comprising a mixing tank in fluidic communication with the anode chamber, wherein the dosing hardware is configured to add the metal-containing material to the anolyte in the mixing tank, wherein the mixing tank comprises a level sensor for sensing a level of anolyte in the mixing tank, and wherein the controller is configured to cause introduction of the metal-containing material from the dosing hardware to the anolyte in the mixing tank based at least in part on input from the level sensor on the mixing tank.
10. The system of claim 3, further comprising a differential pressure sensor configured to measure a pressure differential between anolyte entering the filter and anolyte exiting the filter.
11. The system of claim 1, wherein the system comprises a plurality of electroplating cells and one or more anolyte reservoir.
12. The system of claim 1, wherein the dosing hardware comprises a cartridge comprising the metal-containing material therein, wherein the cartridge is configured to receive anolyte and expose the anolyte to the metal-containing material.
13. The system of claim 12, wherein the metal-containing material comprises porous media formed by sintering one or more metal-containing powder.
14. The system of claim 1, further comprising:
a second membrane positioned below the membrane, wherein the second membrane permits

passage of ions from the anode chamber to the cathode chamber during electroplating and prevents passage of organic compounds from the cathode chamber to the anode chamber during electroplating; and

5 a middle chamber positioned below the membrane and above the second membrane, between the cathode chamber and the anode chamber,

wherein an inlet of the dosing hardware is configured to receive anolyte flowing from the anode chamber, and an outlet of the dosing hardware is configured to deliver anolyte flowing toward the middle chamber.

15. A method of electroplating a metal onto a substrate, the method comprising:
10 providing the substrate in an electroplating cell, the electroplating cell comprising:

an anode, wherein the anode is an inert anode,

a cathode chamber configured to hold catholyte and receive the substrate during electroplating such that the substrate is exposed to the catholyte,

an anode chamber configured to hold anolyte and the anode during electroplating,

15 a membrane separating the cathode chamber from the anode chamber, wherein the membrane permits passage of ions from the anode chamber to the cathode chamber during electroplating and prevents passage of organic compounds from the cathode chamber to the anode chamber during electroplating, and

oxidizing the anolyte at the anode to generate hydrogen ions;

20 electroplating the metal onto the substrate; and

exposing the anolyte to a metal-containing material, the metal-containing material comprising a heterogeneous material comprising the metal being electroplated on the substrate, wherein exposing the anolyte to the metal-containing material reacts the hydrogen ions generated at the anode with the metal-containing material to produce metal ions in the anolyte.

25 16. The method of claim 15, wherein the metal-containing material comprises at least one of a metal oxide, a metal hydroxide, a metal carbonate, a metal bicarbonate, or a metal sulfide.

17. The method of claim 15, further comprising filtering the anolyte to remove the metal-containing material from the anolyte.
18. The method of claim 15, further comprising adding the metal-containing material to a mixing tank in fluidic communication with the anode chamber.
- 5 19. The method of claim 18, further comprising flowing a slurry of the anolyte and the metal-containing material in a trunk line from the mixing tank toward the anode chamber.
20. The method of claim 18, wherein the electroplating cell is positioned in a clean room of a semiconductor fabrication facility, and wherein the mixing tank is positioned either (i) outside of the clean room of the semiconductor fabrication facility, or (ii) within a sub-environment within
10 the clean room of the semiconductor fabrication facility, wherein the sub-environment comprises a filter that enables use of powdered material within the sub-environment without contaminating the rest of the clean room.
21. The method of claim 18, further comprising measuring a level of anolyte in the mixing tank with a level sensor, and adding the metal-containing material to the mixing tank based at
15 least in part on the measured level of anolyte in the mixing tank.
22. The method of claim 15, further comprising flowing the anolyte through a filter, and sensing a differential pressure between anolyte entering the filter and anolyte exiting the filter.
23. The method of claim 15, wherein exposing the anolyte to the metal-containing material comprises flowing the anolyte through a cartridge comprising the metal-containing material.
- 20 24. A cartridge for providing a metal-containing material to anolyte during electroplating, the cartridge comprising:
- an inlet configured to receive anolyte;
- an outlet configured to deliver anolyte;
- an internal fluid path connecting the inlet to the outlet; and
- 25 a metal-containing material comprising a metal and at least one other element, wherein anolyte passing through the internal fluid path is exposed to the metal-containing material.

25. The cartridge of claim 24, wherein the metal-containing material comprises copper oxide provided as pellets and/or puck-shaped elements, the pellets and/or puck-shaped elements having a porosity between about 20% and about 60%.