

ELECTROPLATING AQUEOUS SOLUTION AND METHOD OF MAKING AND USING SAME

TECHNICAL FIELD

[1] Embodiments of the invention relate to an electroplating aqueous solution for electroplating copper, a method of making such an electroplating aqueous solution, and a method of electroplating copper onto a substrate.

BACKGROUND

[2] Copper-based materials have currently supplanted aluminum-based materials as the material of choice for interconnects in integrated circuits ("ICs"). Copper offers a lower electrical resistivity and a higher electromigration resistance than that of aluminum, which has historically been the dominant material used for interconnects.

[3] Interconnects in an IC are becoming one of the dominant factors for determining system performance and power dissipation. For example, the total length of interconnects in many currently available ICs can be twenty miles or more. At such lengths, interconnect resistance-capacitance ("RC") time delay can exceed a clock cycle and severely impact device performance. Additionally, the interconnect RC time delay also increases as the size of interconnects continues to relentlessly decrease with corresponding decreases in transistor size. Using a lower resistivity material, such as copper, decreases the interconnect RC time delay, which increases the speed of ICs that employ interconnects formed from copper-based materials. Copper also has a thermal conductivity that is about two times aluminum's thermal conductivity and an electromigration resistance that is about ten to about one-hundred times greater than that of aluminum.

[4] Copper-based interconnects have also found utility in other applications besides ICs. For example, solar cells, flat-panel displays, and many other types of electronic devices can benefit from using copper-based interconnects for the same or similar reasons as ICs.

[5] Due to difficulties uniformly depositing and void-free filling trenches and other small features with copper using physical vapor deposition ("PVD") and chemical vapor deposition ("CVD"), copper interconnects are typically fabricated using a Damascene process. In the Damascene process, a trench is formed in, for example, an interlevel dielectric layer, such as a carbon-doped oxide. The dielectric layer is covered with a barrier layer formed from, for example, tantalum or titanium nitride to prevent copper from diffusing into the silicon substrate and degrading transistor performance. A seed layer is formed on the barrier layer to promote uniform deposition of copper within the trench. The substrate is immersed in an electroplating aqueous solution that includes copper. The substrate functions as a cathode of an electrochemical cell in which the electroplating aqueous solution functions as an electrolyte, and the copper from the electroplating aqueous solution is electroplated in the trench responsive to a voltage applied between the substrate and an anode. Then, copper deposited on regions of the substrate outside of the trench is removed using chemical-mechanical polishing ("CMP").

[6] Regardless of the particular electronic device in which copper is used as a conductive structure, it is important that an electroplating process for copper be sufficiently fast to enable processing a large number of substrates and have an acceptable yield. Additionally, the cost of the electroplating aqueous solution is also another factor impacting overall fabrication cost of electronic devices using copper. This is particularly important in the fabrication of solar cells, which have to cost-effectively compete with other, potentially more cost-effective, energy generation technologies. Thus, it is desirable that copper electroplating aqueous solutions be capable of depositing copper in a uniform manner (*i.e.*, high throwing power) and at a high-deposition rate.

[7] A number of electroplating aqueous solutions are currently available for electroplating copper. For example, sulfate-based electroplating

aqueous solutions are commonly used for electroplating copper. Some alkaline copper electroplating aqueous solutions have a high-throwing power, but are not capable of rapidly depositing copper without compromising the deposited film quality. At high-deposition rates, the copper may grow as dendrites as opposed to a more uniformly deposited film. Additionally, alkali elements (e.g., sodium and potassium) in such alkaline copper electroplating aqueous solutions can diffuse into silicon substrates and are deep-level impurities in silicon that can compromise transistor performance. Fluoroborate electroplating aqueous solutions can be used for high-speed deposition of copper. However, fluoroborate electroplating aqueous solutions can be more expensive than, more traditional, sulfate-based solutions. Moreover, fluoroborate electroplating aqueous solutions may be more hazardous and difficult to dispose of than many other electroplating aqueous solutions for electroplating copper.

[8] Therefore, there is still a need for an electroplating aqueous solution for electroplating copper that can deposit a high-quality film of copper at a high-speed.

SUMMARY

[9] In one embodiment of the invention, an electroplating aqueous solution is disclosed. The electroplating aqueous solution includes at least two acids, copper, at least one accelerator agent, and at least two suppressor agents. The at least one accelerator agent provides an acceleration strength of at least about 2.0 and the at least two suppressor agents, collectively, provide a suppression strength of at least about 5.0.

[10] In another embodiment of the invention, a method of electroplating is disclosed. A substrate is immersed in an electroplating aqueous solution. The electroplating aqueous solution includes at least two acids, copper, at least one accelerator agent, and at least two suppressor agents. The at least one accelerator agent provides an acceleration strength of at least about 2.0 and the at least two suppressor agents, collectively, provide a

suppression strength of at least about 5.0. At least a portion of the copper from the electroplating aqueous solution is electroplated onto the substrate.

[11] In yet another embodiment of the invention, a method of making an electroplating aqueous solution is disclosed. An electroplating aqueous solution maintained at a first temperature may be provided. The electroplating aqueous solution includes at least two acids and copper present in a concentration below a copper solubility limit, at the first temperature, of the at least two acids. The electroplating aqueous solution is heated to a second temperature that is greater than the first temperature. Additional copper from a copper source is introduced into the electroplating aqueous solution when the electroplating aqueous solution is at the second temperature so that the electroplating aqueous solution exhibits a copper concentration of at least about 50 grams per liter.

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BRIEF DESCRIPTION OF THE DRAWINGS

[12] The drawings illustrate various embodiments of the invention, wherein like reference numerals refer to like elements or features in different views or embodiments shown in the drawings.

[13] **FIGS. 1A** and **1B** are schematic cross-sectional views of an electroplating system that may be used for practicing embodiments for electroplating copper onto a substrate according to various methods of the invention.

[14] **FIG. 2** is graph illustrating an example of a forward-pulse current density waveform that may be used to electroplate copper from any of the disclosed electroplating aqueous solutions.

[15] **FIG. 3** is graph illustrating an example of a reverse-pulse current density waveform that may be used to electroplate copper from any of the disclosed electroplating aqueous solutions.

DETAILED DESCRIPTION

- [16] Embodiments of the invention are directed to electroplating aqueous solutions for electroplating copper, methods of making such electroplating aqueous solutions, and methods of electroplating copper onto a substrate using such electroplating aqueous solutions. The disclosed electroplating aqueous solutions may be used for electroplating copper onto a substrate as a film that is substantially-free of dendrites and at a high-deposition rate (e.g., about 10 μm per minute or more) for forming electrical interconnects used in ICs, solar cells, and many other applications.
- [17] According to various embodiments of the invention, an electroplating aqueous solution includes at least two acids, copper in the form of cupric ions (Cu^{2+}), at least one accelerator agent that provides an acceleration strength of at least about 2.0, and at least two suppressor agents that collectively provide a suppression strength of at least about 5.0. The at least two acids and the copper collectively form an electrolyte. The at least two acids may be selected from two or more of the following acids: sulfuric acid, hydrochloric acid, hydroiodic acid, hydroboric acid, fluoroboric acid, and any other suitable acid. In a more specific embodiment of the invention, the at least two acids includes sulfuric acid present in a concentration from about 5 grams per liter ("g/L") to about 20 g/L and hydrochloric acid present in a concentration from about 20 mg/L to about 100 mg/L. In addition to the aforementioned at least two acids, in certain embodiments of the invention, the electroplating aqueous solution may further include a supplemental acid selected to increase the solubility of the copper in the at least two acids of the electroplating aqueous solution. For example, the supplemental acid may be selected from alkane sulfonic acid, methane sulfonic acid, ethane sulfonic acid, propane sulfonic acid, butane sulfonic acid, pentane sulfonic acid, hexane sulfonic acid, decane sulfonic acid, dedecane sulfonic acid, fluoroboric acid, mixtures of any of the preceding supplemental acids, or another suitable acid selected to

increase the solubility of the copper in the at least two acids of the electroplating aqueous solution.

[18] The copper may be present in the electroplating aqueous solution in a concentration of at least about 50 g/L and, more particularly, from about
5 50 g/L to about 100 g/L. In a more specific embodiment of the invention, the concentration of the copper may be at least about 85 g/L to about 100 g/L.

[19] As discussed above, the electroplating aqueous solution includes additives, such as suppressor and accelerator agents that improve certain
10 electroplating characteristics of the electroplating aqueous solution. As used throughout this disclosure and claims, the phrase “virgin make solution” (“VMS”) refers to an electroplating aqueous solution without any suppressor agents and accelerator agents. For the electroplating aqueous solution embodiments described herein, the VMS includes the at least two
15 acids and the copper dissolved therein. As used throughout this disclosure and claims, “suppression strength” of one or more suppressor agents of an electroplating aqueous solution is determined by a decrease in current density at a cathode of an electrochemical cell that includes a suppressed solution containing VMS and the one or more suppressor agents compared
20 to current density at a cathode of an electrochemical cell that includes a solution containing generally only the VMS, with each current density measured at about -0.7 volts relative to a mercurous sulfate electrode (“MSE”). For the electroplating aqueous solution embodiments described herein, a suppressed solution includes the at least two acids, the copper,
25 and the at least two suppressor agents. As merely an example, when a current density at a cathode of an electrochemical cell utilizing a suppressed solution is five times lower than a current density of an electrochemical cell utilizing a VMS, a suppressor agent provides a suppression strength of 5.0.

[20] As used throughout this disclosure and claims, "acceleration strength" of one or more accelerator agents of an electroplating aqueous solution is measured by an increase in current density at a cathode of an electrochemical cell that includes an accelerated solution containing VMS and the one or more accelerator agents compared to current density at a cathode of an electrochemical cell that includes the above-described suppressed solution, with each current density measured at about -0.7 volts relative to a MSE. For the electroplating aqueous solution embodiments described herein, an accelerated solution includes the at least two acids, the copper, and the at least one accelerator agent. As merely an example, when a current density at a cathode of an electrochemical cell utilizing an accelerated solution is two times higher than a current density of an electrochemical cell utilizing a suppressed solution, an accelerator agent provides acceleration strength of 2.0.

[21] The at least one accelerator agent of the electroplating aqueous solution is formulated to increase the deposition rate of copper onto a substrate and present in the electroplating aqueous solution in an amount sufficient to provide an acceleration strength of at least about 2.0. The at least one accelerator agent may further increase the brightness of the electroplated copper film and other qualities, such as decreasing void concentration in the electroplated copper film. The at least one accelerator agent may be present in the electroplating aqueous solution in concentration from about 10 mg/L to about 1000 mg/L. According to various embodiments of the invention, the at least one accelerator agent may be selected from an organic sulfide compound, such as bis (sodium-sulfopropyl) disulfide, 3-mercapto-1-propanesulfonic acid sodium salt, N,N-dimethyl-dithiocarbamyl propylsulfonic acid sodium salt, 3-S-isothiuronium propyl sulfonate, or mixtures of any of the preceding chemicals. Additional suitable accelerator agents include, but are not limited to, thiourea, allylthiourea, acetylthiourea, pyridine, mixtures of any of the preceding

chemicals, or another suitable accelerator agent. The at least one accelerator may also comprise an inorganic compound selected to increase the deposition rate of the copper from the electroplating aqueous solution, decrease hydrogen evolution that can increase the porosity in the electroplated copper film, or both. For example, suitable inorganic compounds may comprise selenium-containing anions (e.g., SeO_3^{2-} and Se^{2-}), tellurium-containing anions (e.g., TeO_3^{2-} and Te^{2-}), or both. Additionally, many of the disclosed accelerator agents may be substantially-free of alkali elements (e.g., sodium and potassium), which can be detrimental to the performance of semiconductor devices used in ICs. Accordingly, a copper film deposited from one of the disclosed electroplating aqueous solutions having an accelerator agent that is substantially free of alkali elements will also be substantially-free of alkali elements.

[22] The at least two suppressor agents of the electroplating aqueous solution are formulated to substantially suppress formation of dendrites during electroplating copper from the electroplating aqueous solution and improve other qualities of an electroplated copper film, such as surface roughness, ductility, brightness, and electrical conductivity. The at least two suppressor agents may be, collectively, present in the electroplating aqueous solution in concentration from about 10 mg/L to about 1000 mg/L. Together, the at least two suppressor agents are present in the electroplating aqueous solution in an amount sufficient to provide a suppression strength of at least about 5.0. The suppressor agents may be a surfactant, a leveler agent, a wetting agent, a chelating agent, or an additive that exhibits a combination of any of the foregoing functionalities. The at least two suppressor agents may be selected from two or more of the following suppressor agents: a quaternized polyamine, a polyacrylamide, a cross-linked polyamide, a phenazine azo-dye (e.g., Janus Green B), an alkoxylated amine surfactant, a polyether surfactant, a

non-ionic surfactant, a cationic surfactant; an anionic surfactant, a block copolymer surfactant, polyacrylic acid, a polyamine, aminocarboxylic acid, hydrocarboxylic acid, citric acid, entprol, edetic acid, tartaric acid, and any other suitable suppressor agent.

5 **[23]** The electroplating aqueous solutions may be manufactured according to a number of different embodiments. According to one embodiment of the invention, a container may be provided that contains an electrolyte including the at least two acids and copper dissolved in the at least two acids. The electrolyte is maintained at a first temperature that
10 may be, for example, about room temperature (e.g., about 20 °C). The copper may be present in the electrolyte in a concentration that is at or below a solubility limit, at the first temperature, of the copper in the electrolyte. For example, the copper may be present in the electrolyte in a concentration that is at or below 50 g/L. Next, the electrolyte is heated to a
15 second temperature that is greater than the first temperature. At the second temperature, the copper has a higher solubility in the electrolyte. The second temperature may be a temperature at which a copper electroplating process may be performed, such as about 50 °C or more.

20 **[24]** Then, additional copper from a copper source is added to the electrolyte while the electrolyte is maintained at the second temperature. The copper source may be one or more of the following copper sources: a copper salt (e.g., copper sulfate), copper oxide, and copper hydroxide. The amount of the additional copper may be selected so that the copper concentration in the electrolyte is at or approaches the copper solubility
25 limit, at the second temperature, for the electrolyte. For example, the additional copper may be added to the electrolyte to increase the copper concentration thereof to about 50 g/L to about 100 g/L. In certain embodiments of the invention, the additional copper may be added to the electrolyte so that the copper concentration of the electrolyte, at the
30 second temperature, is at least about 85 g/L. The at least one accelerator

agent and the at least two suppressor agents may be mixed with the electrolyte prior to heating the electrolyte to the second temperature or after adding the additional copper.

[25] When precipitation of copper is not a concern, the electroplating aqueous solution may be formulated merely by mixing the selected at least two acids, copper salt, at least one accelerator agent, and the at least two suppression agents. For example, when the fluoroboric acid comprises one of the at least two acids, the solubility of copper therein is sufficiently high at room temperature so that additional copper does not need to be added at a higher temperature to increase the copper concentration to a desired level.

[26] FIG. 1A is a schematic cross-sectional view of an electroplating system **100** that may be used for practicing embodiments for electroplating copper onto a substrate according to various methods of the invention. The electroplating system **100** may include a number of linearly spaced and isolated containers. However, in other configurations, the containers may be radially spaced and isolated from each other. For example, the electroplating system **100** may include a cleaning container **101** holding a cleaning solution **102**, a rinse container **103** holding a rinsing solution **104** (e.g., water), an electroplating container **105** holding an electroplating aqueous solution **106** that may be any of the previously described embodiments of electroplating aqueous solutions, a post-plating cleaning container **107** holding a post-plating cleaning solution **108**, and a drying container **109** for drying a plated substrate after cleaning in the post-plating cleaning container **107**. For example, the cleaning solution **102** may include one or more suppressor agents. In one embodiment of the invention, the one or more suppressor agents of the cleaning solution **102** may have the same composition of one of the suppressor agents used in the electroplating aqueous solution **106**. The drying container **109** may hold a drying solution **110** (e.g., isopropyl alcohol ("IPA") in water or other

drying solution) to effect removal any post-plating cleaning solution **108** on the substrate or the substrate may be spin dried. Although not shown, external heaters may maintain the temperature of the electroplating aqueous solution **106** disposed within the electroplating container **105** at a
5 selected electroplating temperature, such as between about 20 °C to about 60 °C.

[27] The electroplating system **100** further includes an actuator system **111** that is operably coupled to a substrate holder **112** via a movable arm **114**. The actuator system **111** is operable to controllably and selectively
10 move the substrate holder **112** upwardly and downwardly in vertical directions V_1 and V_2 and horizontally in horizontal directions H_1 and H_2 . The substrate holder **112** is configured to hold a substrate **116** having a surface **117** on which a copper film **119** is electroplated and further includes provisions, such as electrical contact pins, that electrically contact
15 the substrate **116**. It should be emphasized that any suitable substrate holder **114** may be used. Although only a single substrate is illustrated in **FIG. 1A** for simplicity, many commercially available substrate holders are configured to hold multiple substrates. Additionally, the term “substrate” refers to any workpiece capable of being electroplated. For example,
20 suitable substrates include, but are not limited to, semiconductor substrates (e.g., single-crystal silicon wafers, single-crystal gallium arsenide wafer, etc.) with or without active and/or passive devices (e.g., transistors, diodes, capacitors, resistors, etc.) formed therein, printed circuit boards, flexible polymeric substrates, and many other types of
25 substrates. Additionally, a variety of different fluid supply systems may be employed to supply the various fluids in the containers **101**, **103**, **105**, **107**, and **109** and, optionally, to re-circulate the electroplating aqueous solution **106** to provide a generally laminar flow of the electroplating aqueous solution **106** over the substrate **116**. Such fluid supply systems and
30 container configurations are well-known and in the interest of brevity are

not described in detail herein. Referring to **FIG. 1B**, in other configurations, the substrate holder **112** may be positioned so that the surface **117** of the substrate **116** is oriented in a downward direction (as shown) or an upward direction, and the actuator system **111** is operable to rotate the substrate holder **112** and substrate **116** in a direction **R**.

[28] The electroplating system **100** further includes a voltage source **118** that is electrically connected to the substrate holder **112** (*i.e.*, the cathode) and consequently, the substrate **116**. The voltage source **118** is further electrically connected to an anode **120** immersed in the electroplating aqueous solution **106** of the electroplating bath **105**. The anode **120** may be spaced a distance **S** from the surface **117** of the substrate **116**. For example, the distance **S** may be about 0.1 centimeters ("cm") to about 10 cm and, more specifically about 1 cm. The voltage source **118** is operable to apply a selected voltage between the substrate **116** and the anode **120**.

[29] Various embodiments of methods of the invention for electroplating copper onto the substrate **116** will now be discussed below in more detail in conjunction with **FIGS. 1A** and **1B**. In practice, the actuator system **111** may immerse the substrate holder **112** carrying the substrate **116** into the cleaning solution **102**, followed by immersing the substrate holder **112** carrying the substrate **116** into the rinsing solution **104**. Next, the actuator system **111** may immerse the substrate holder **112** carrying the substrate **116** into the electroplating aqueous solution **106**. While the substrate **116** immersed in the electroplating aqueous solution **106**, the voltage source **118** may apply a voltage between the substrate **116** and the anode **120** to cause copper from the electroplating aqueous solution **106** to plate onto surface **117** of the substrate **116** to form the copper film **119**.

[30] While the substrate **116** is immersed in the electroplating aqueous solution **106** and copper is being electroplated onto the surface **117** of the substrate **116**, the actuator system **111** may move the substrate holder **112**

and the substrate **116** in a linear oscillatory manner in the directions V_1 and V_2 . For example, the substrate **116** may be linearly oscillated at a rate of about 10 millimeters per second ("mm/s") to about 1000 mm/s and with a stroke length of about 600 mm. In one embodiment of the invention, when
5 the substrate **116** has a diameter of about 300 mm, the substrate **116** is linearly oscillated at a frequency of about 100 strokes/min. In some embodiments of the invention, the stroke length may be equal to or greater than dimension D of surface **117** to be electroplated.

[31] With reference to **FIG. 1B**, in another embodiment of the invention,
10 the substrate holder **116** and substrate **112** may be rotated in the direction R as a unit while the surface **117** of the substrate **116** is maintained generally parallel to a longitudinal axis of the anode **120**. For example, the substrate holder **116** and substrate **112** may be rotated in the direction R as a unit at a rotational speed of about 150 revolutions per minute ("RPM")
15 to about 300 RPM and, more particularly, about 200 RPM. In other embodiments of the invention, a combination of linear oscillatory movement of the substrate holder **112** and substrate **116** as a unit in the directions H_1 and H_2 and rotational movement in the direction R may be used. Utilizing any of the above-described techniques for linearly
20 oscillating and/or rotating the substrate **112** enables increasing the limiting current density at the substrate **116** that is limited by diffusion of cupric ions within the electroplating aqueous solution **106** to the surface **117** of the substrate **116**. Consequently, increasing the current density at the substrate **116** increases the electroplating deposition rate of the copper
25 film **119**. For example, utilizing any of the above substrate-movement techniques in combination with the chemistry of the electroplating aqueous solution **106** enables the voltage source **118** to impose a current density at the substrate **116** of about 200 milliamps per square centimeter ("mA/cm²") to about 2000 mA/cm². At such high current densities, the deposition rate
30 of copper onto the surface **117** of the substrate **116** may be 10 μm per

minute or more. Furthermore, the deposited copper film **119** may be substantially dendrite-free despite being deposited at such a high-deposition rate.

[32] When the anode **120** is an inert anode, copper can be continually added to the electroplating aqueous solution **106** to maintain a generally constant concentration of copper as the copper film **119** is deposited. When the anode **120** is a consumable copper anode, copper from the anode **120** may be oxidized and dissolved in the electroplating aqueous solution **106** to maintain a generally constant concentration of copper as the copper film **119** is deposited.

[33] In certain embodiments of the invention, the voltage source **118** may apply a time-varying voltage to impose a forward-pulse current density on the substrate **116** to promote forming a finer grain size in the copper film **119**. For example, **FIG. 2** shows one example of a forward-pulse current density waveform **200** that may be imposed on the substrate **116** by applying a voltage between the substrate **116** and the anode **120** using the voltage source **118**. Representative current densities at the substrate **112** (*i.e.*, the cathode) for the forward-pulse current density waveform **200** may be about 200 mA/cm² to about 2000 mA/cm². In other embodiments of the invention, the voltage source **118** may apply a time-varying voltage to impose a reverse-pulse current density waveform on the substrate **116** or a combination of a forward-pulse and reverse-pulse current density waveform. For example, **FIG. 3** shows one example of a forward-pulse/reverse-pulse current density waveform **300** in which the current density at the substrate **116** may be periodically reversed. Representative current densities at the substrate **112** (*i.e.*, the cathode) for the forward pulse of the forward-pulse/reverse-pulse current density waveform **300** may be increased to about 10 A/cm² with a pulse duration, *t*, of about 0.1 ms to about 100 ms.

[34] After electroplating the copper film **119** onto the substrate **116**, the actuator system **111** may move and immerse the substrate holder **112** and substrate **116** into the post-plating cleaning solution **108** of the post-plating cleaning container **107**. Then, the actuator system **111** may move and
5 immerse the substrate holder **112** and substrate **116** into the drying solution **110** of the drying container **109**.

[35] The disclosed electroplating aqueous solutions may be used for electroplating a high-quality copper film at a high-deposition rate to form many different types of electrically conductive structures. For example,
10 copper electroplated according to methods disclosed herein may be used to form interconnects for ICs using a Damascene process. Copper electroplated according to methods disclosed herein may also be used to form through-substrate interconnects, through-mask plated films, electroplated bumps for flip-chip type electrical connections, or other
15 metallization structures in ICs and other electronic devices. Moreover, copper electroplated according to methods disclosed herein may also be used to form electrical contacts for solar cells. The foregoing, non-limiting, list of applications merely provides some examples of uses of copper electroplated according to methods disclosed herein.

20 [36] From the foregoing it will be appreciated that, although specific embodiments of the invention have been described herein for purposes of illustration, various modifications may be made without deviating from the spirit and scope of the invention.

CLAIMS

1. An electroplating aqueous solution, comprising:
at least two acids;
5 copper;
at least one accelerator agent that provides an acceleration
strength of at least about 2.0; and
at least two suppressor agents that collectively provide a
suppression strength of at least about 5.0.
- 10 2. The electroplating aqueous solution of claim 1 wherein
the at least two acids comprise one or more of the following acids:
sulfuric acid;
hydrochloric acid;
hydroiodic acid;
15 hydroboric acid; and
fluoroboric acid.
3. The electroplating aqueous solution of claim 1 wherein
the at least two acids comprise:
sulfuric acid present in a concentration from about 5 grams per
20 liter to about 20 grams per liter; and
hydrochloric acid present in a concentration from about 20
milligrams per liter to about 100 milligrams per liter.
4. The electroplating aqueous solution of claim 1 wherein
the copper is present in a concentration from about 50 grams per liter to
25 about 100 grams per liter.
5. The electroplating aqueous solution of claim 1 wherein
the concentration is at least about 85 grams per liter.
6. The electroplating aqueous solution of claim 1 wherein
the at least one accelerator agent comprises at least one of:

a sulfide compound;
a selenium-containing anion; and
a tellurium-containing anion.

7. The electroplating aqueous solution of claim 1 wherein
5 the at least two suppressor agents comprise one or more of the following
suppressor agents:

a surfactant;
a chelating agent;
a leveler agent; and
10 a wetting agent.

8. The electroplating aqueous solution of claim 1 wherein
the at least two suppressor agents comprise one or more of the following
suppressor agents:

a quaternized polyamine; a polyacrylamide; a cross-linked
15 polyamide;
a phenazine azo-dye; an alkoxyated amine surfactant; a
polyether surfactant; a non-ionic surfactant; a cationic
surfactant; an anionic surfactant; a block copolymer
surfactant; polyacrylic acid; a polyamines; aminocarboxylic
20 acid;
hydrocarboxylic acid; citric acid; entprol; edetic acid; and
tartaric acid.

9. The electroplating aqueous solution of claim 1 wherein:
the at least one accelerator agent is present in a concentration
25 from about 10 milligrams per liter to about 1000 milligrams per liter; and
the at least two suppressor agents are collectively present in a
concentration from about 10 milligrams per liter to about 1000 milligrams
per liter.

10. The electroplating aqueous solution of claim 1 wherein:
the at least two acids are, collectively, present in a
concentration from about 5 grams per liter to about 20 grams per liter; and
the copper is present in a concentration from about 50 grams
5 per liter to about 100 grams per liter.

11. A method of electroplating, comprising:
immersing a substrate in an electroplating aqueous solution,
the electroplating aqueous solution comprising:
at least two acids;
10 copper;
at least one accelerator agent that provides an
acceleration strength of at least about 2.0; and
at least two suppressor agents that collectively provide
a suppression strength of at least about 5.0; and
15 electroplating at least a portion of the copper from the
electroplating aqueous solution onto the substrate.

12. The method of claim 11, further comprising linearly
oscillating the substrate in the electroplating aqueous solution during the
act of electroplating.

20 13. The method of claim 12 wherein linearly oscillating the
substrate in the electroplating aqueous solution comprises:
linearly oscillating the substrate in the bath at a rate of about
10 millimeters per second to about 1000 millimeters per second.

14. The method of claim 11, further comprising rotating the
25 substrate in the electroplating aqueous solution during the act of
electroplating.

15. The method of claim 14 wherein rotating the substrate in
the electroplating aqueous solution comprises:

rotating the substrate in the electroplating aqueous solution at a rate of about 150 revolutions per minute to about 300 revolutions per minute.

16. The method of claim 14:

5 wherein the substrate comprises a surface to be electroplated with the copper; and

further comprising orienting the surface in an upwardly facing direction or downwardly facing direction.

17. The method of claim 14:

10 wherein the substrate comprises a surface to be electroplated with the copper;

further comprising moving the substrate in a manner that maintains the surface substantially parallel to a longitudinal axis of an anode immersed in the electroplating aqueous solution.

15 18. The method of claim 11 wherein electroplating at least a portion of the copper from the electroplating aqueous solution onto the substrate comprises:

20 depositing the copper on the substrate as a substantially dendrite-free film at a deposition rate of at least 10 micrometers per minute.

19. The method of claim 11, further comprising adding additional copper to the electroplating aqueous solution provided from a consumable anode immersed in the electroplating aqueous solution.

25 20. The method of claim 11, further comprising replenishing the electroplating aqueous solution with additional copper introduced into the electroplating aqueous solution.

21. The method of claim 11, further comprising:

prior to immersing the substrate in the electroplating aqueous solution, cleaning the substrate in a cleaning solution that includes at least one suppressor agent having the same composition as one of the at least two suppressor agents of the electroplating aqueous solution.

5 22. The method of claim 11, further comprising maintaining the electroplating aqueous solution at a temperature between about 20 °Celsius to about 60 °Celsius.

 23. The method of claim 11:
 wherein the substrate comprises a surface to be electroplated
10 with the copper; and

 further comprising spacing the surface a distance of about 0.1 centimeter to about 10 centimeter from an anode immersed in the electroplating aqueous solution.

 24. The method of claim 11 wherein the at least two acids of
15 the electroplating aqueous solution comprise one or more of the following acids:

 sulfuric acid;
 hydrochloric acid;
 hydroiodic acid;
20 hydroboric acid; and
 fluoroboric acid.

 25. The method of claim 11 wherein the at least two acids of the electroplating aqueous solution comprise:

 sulfuric acid present in a concentration from about 5 grams per
25 liter to about 20 grams per liter; and
 hydrochloric acid present in a concentration from about 20 milligrams per liter to about 100 milligrams per liter.

26. The method of claim 11 wherein the copper of the electroplating aqueous solution is present in a concentration from about 50 grams per liter to about 100 grams per liter.

27. The method of claim 11 wherein the at least one
5 accelerator agent of the electroplating aqueous solution comprises at least one of:

a sulfide compound;
a selenium-containing anion; and
a tellurium-containing anion.

10 28. The method of claim 11 wherein the at least two suppressor agents of the electroplating aqueous solution comprise one or more of the following suppressor agents:

a surfactant;
a chelating agent;
15 a leveler agent; and
a wetting agent.

29. The method of claim 11 wherein the at least two suppressor agents of the electroplating aqueous solution comprise one or more of the following suppressor agents:

20 a quaternized polyamine; a polyacrylamide; a cross-linked polyamide;
a phenazine azo-dye; an alkoxyated amine surfactant; a polyether surfactant; a non-ionic surfactant; a cationic surfactant; an anionic surfactant; a block copolymer
25 surfactant; polyacrylic acid; a polyamines; aminocarboxylic acid;
hydrocarboxylic acid; citric acid; entprol; edetic acid; and tartaric acid.

30. The method of claim 11 wherein:

the at least one accelerator agent is present in a concentration from about 10 milligrams per liter to about 1000 milligrams per liter; and

the at least two suppressor agents are collectively present in a
5 concentration from about 10 milligrams per liter to about 1000 milligrams per liter.

31. The method of claim 11 wherein:

the at least two acids of the electroplating aqueous solution are, collectively, present in a concentration from about 5 grams per liter to
10 about 20 grams per liter; and

the copper of the electroplating aqueous solution is present in a concentration from about 50 grams per liter to about 100 grams per liter.

32. A method of making an electroplating aqueous solution, comprising:

15 maintaining an electroplating aqueous solution at a first temperature, the electroplating aqueous solution including:

at least two acids;

copper present in a concentration below a copper solubility limit, at the first temperature, of the at least two acids;

20 heating the electroplating aqueous solution to a second temperature that is greater than the first temperature; and

introducing additional copper from a copper source to the electroplating aqueous solution when the electroplating aqueous solution is at the second temperature so that the electroplating aqueous solution
25 exhibits a copper concentration of at least about 50 grams per liter.

33. The method of claim 32 wherein introducing additional copper from a copper source comprises:

introducing additional copper in a concentration that is less than a copper solubility limit of the at least two acids at the electroplating temperature.

34. The method of claim 32 wherein introducing additional
5 copper comprises:

introducing the additional copper into the electroplating aqueous solution in an amount so that the copper concentration is about 50 grams per liter to about 100 grams per liter at the second temperature.

35. The method of claim 32 wherein introducing additional
10 copper from a copper source comprises:

introducing the additional copper into the electroplating aqueous solution in an amount so that the copper concentration is about 85 grams per liter or more at the second temperature.

36. The method of claim 32 wherein the copper source
15 comprises at least one of:

a copper salt;
copper oxide; and
copper hydroxide.

37. The method of claim 31 wherein the electroplating
20 aqueous solution comprises at least one accelerator agent that provides an acceleration strength of at least about 2.0 and at least two suppressor agents that collectively provides a suppression strength of at least about 5.0.