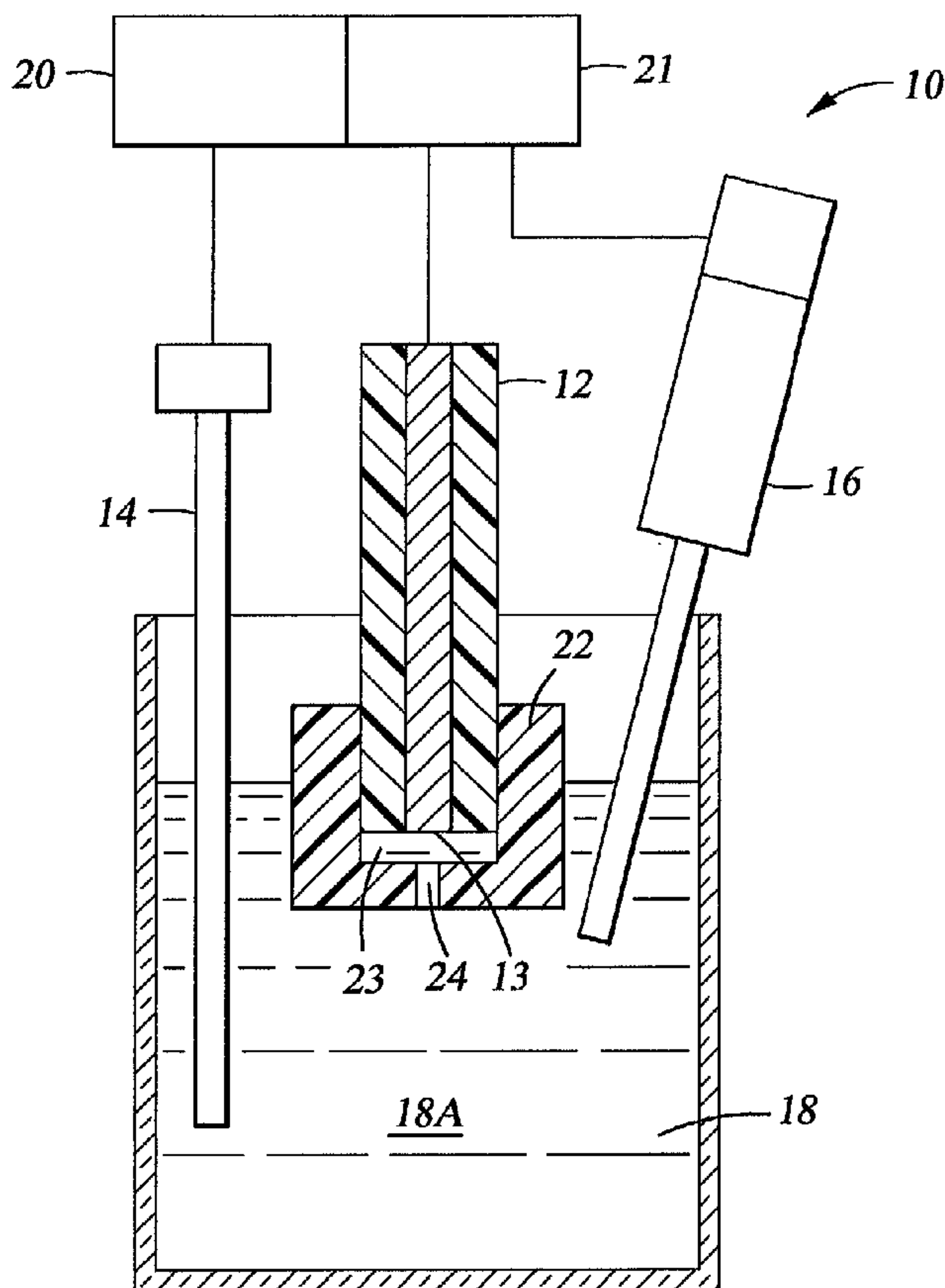




US 20030029726A1

(19) **United States**(12) **Patent Application Publication**
Kovarsky et al.(10) **Pub. No.: US 2003/0029726 A1**(43) **Pub. Date: Feb. 13, 2003**(54) **APPARATUS AND METHOD OF
EVALUATING ELECTROPLATING
SOLUTIONS AND CONDITIONS**(75) Inventors: **Nicolay Kovarsky**, Sunnyvale, CA
(US); **Zhi-Wen Sun**, San Jose, CA
(US); **Girish A. Dixit**, San Jose, CA
(US)Correspondence Address:
APPLIED MATERIALS, INC.
2881 SCOTT BLVD. M/S 2061
SANTA CLARA, CA 95050 (US)(73) Assignee: **Applied Materials, Inc.**(21) Appl. No.: **09/924,080**(22) Filed: **Aug. 7, 2001****Publication Classification**(51) **Int. Cl.⁷** **C25D 21/12; C25D 5/00;**
C25D 17/00(52) **U.S. Cl.** **205/81; 204/230.1**(57) **ABSTRACT**

The present invention generally relates to an apparatus and method of evaluating electroplating solutions and conditions. In one embodiment, the method of evaluating electroplating solutions comprises utilizing an electrochemical measuring cell having a working electrode having a lid with at least one hole, a counter electrode, and a reference electrode. The working electrode, the counter electrode, and the reference electrode are immersed in at least one sample of at least one electroplating solution. The lid is disposed over the working electrode forming a chamber between the working electrode and the lid. The lid further has a hole to allow an electroplating solution to flow into the chamber and reach the working electrode. The potential of the working electrode in the sample of the electroplating solution is measured over time with a constant current supplied to the working electrode. The electrochemical measurements may be used to determine which solutions are capable of bottom-up filling and may be used to estimate the optimal electroplating parameters. In still another embodiment, the present invention relates to an apparatus for electroplating a substrate comprises a chamber body, an anode disposed in the chamber body, a contact ring disposed in the chamber body, one or more power supplies coupled to the anode and the contact ring, and an electrochemical measuring cell disposed in the chamber body or coupled to an electrolyte output coupled to the chamber body.



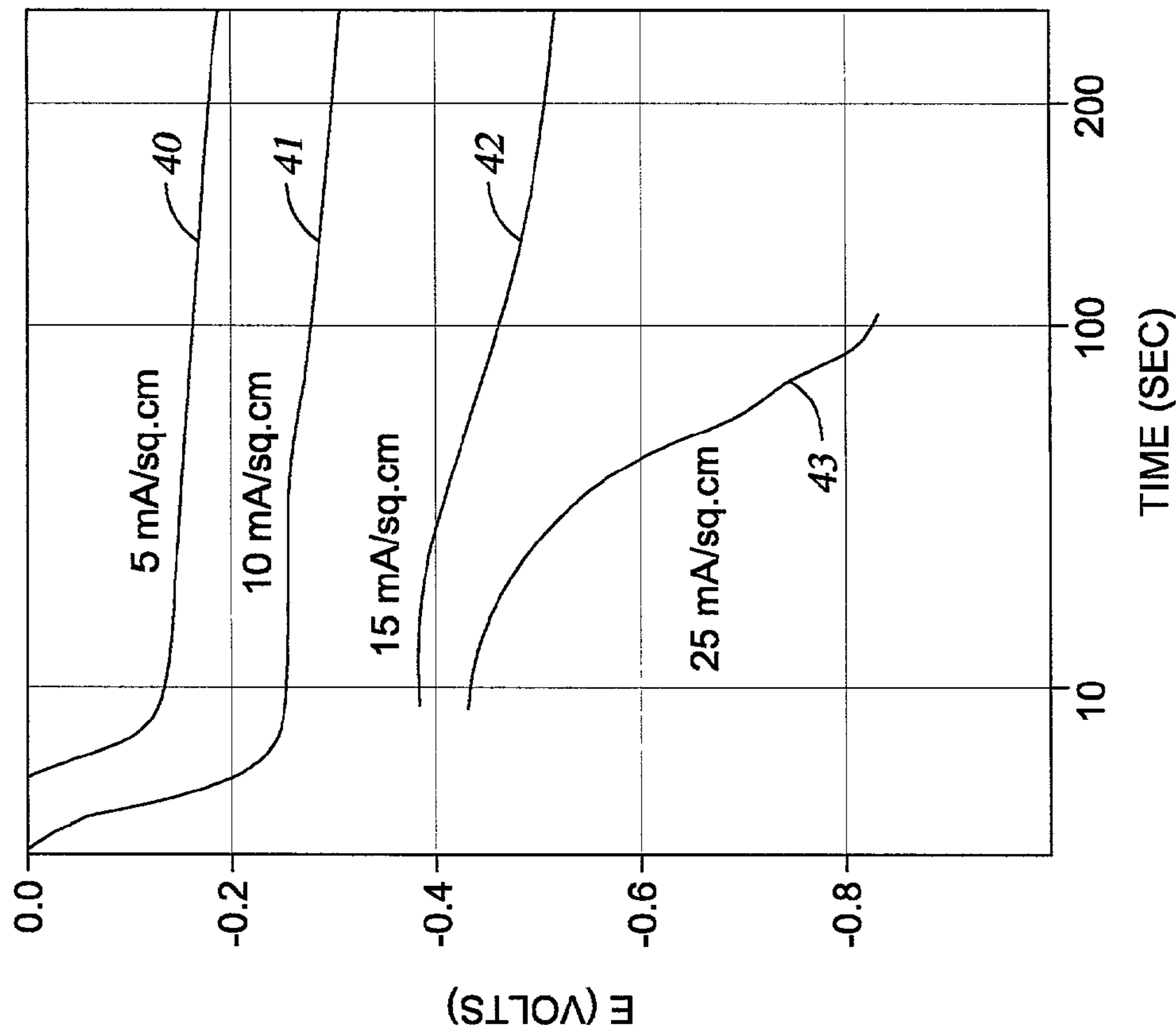


Fig. 4

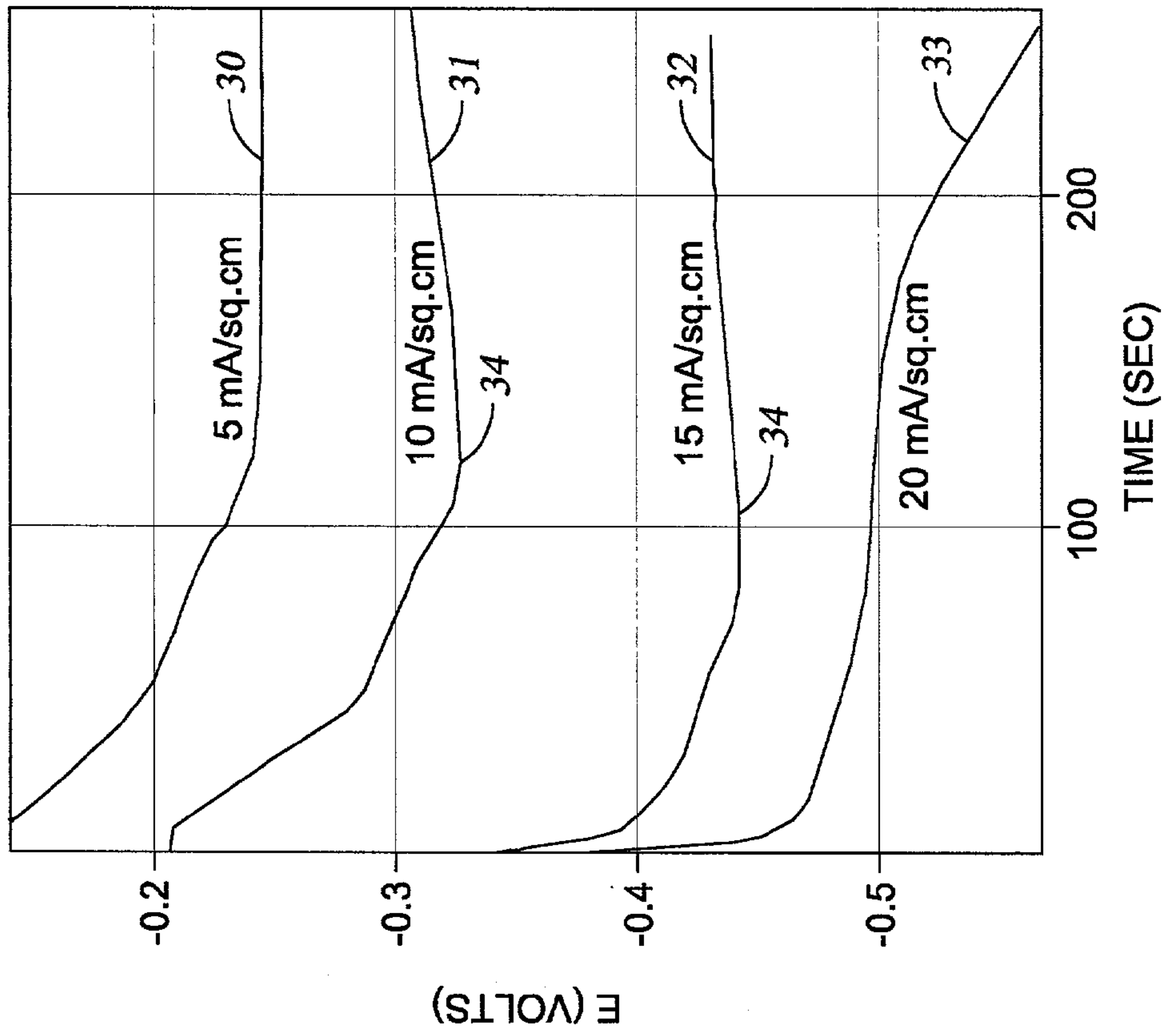


Fig. 3

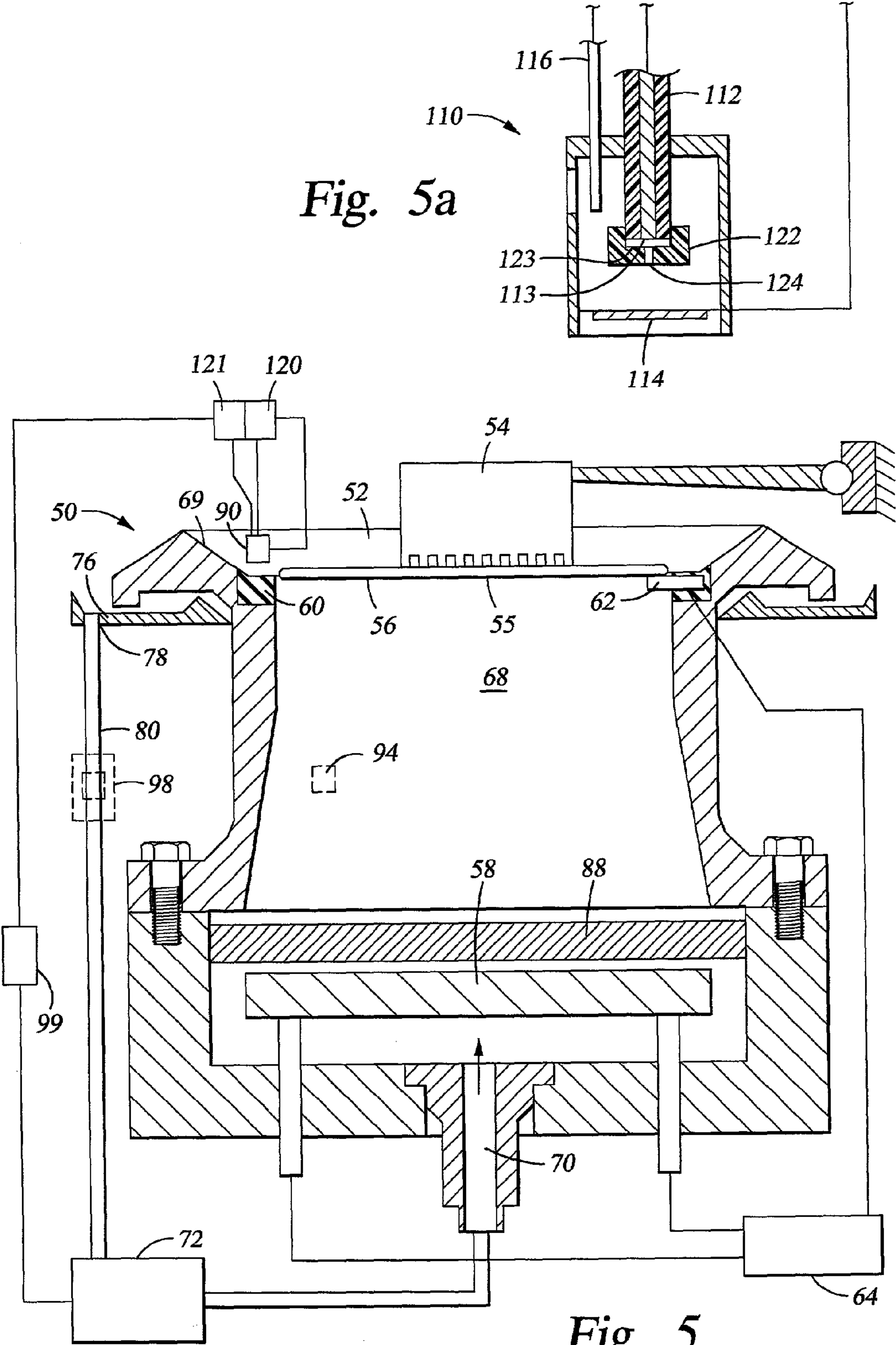


Fig. 6a

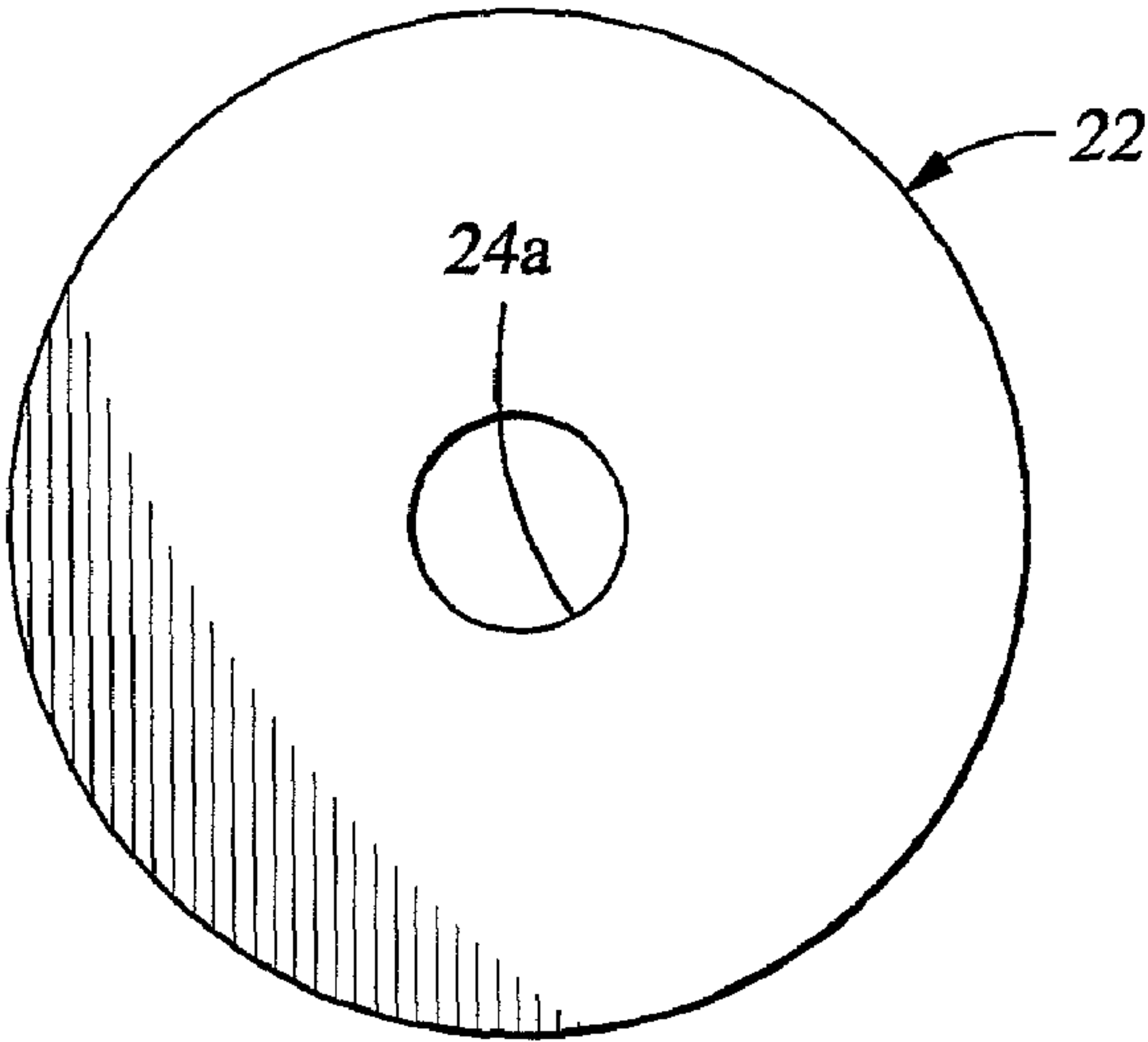


Fig. 6b

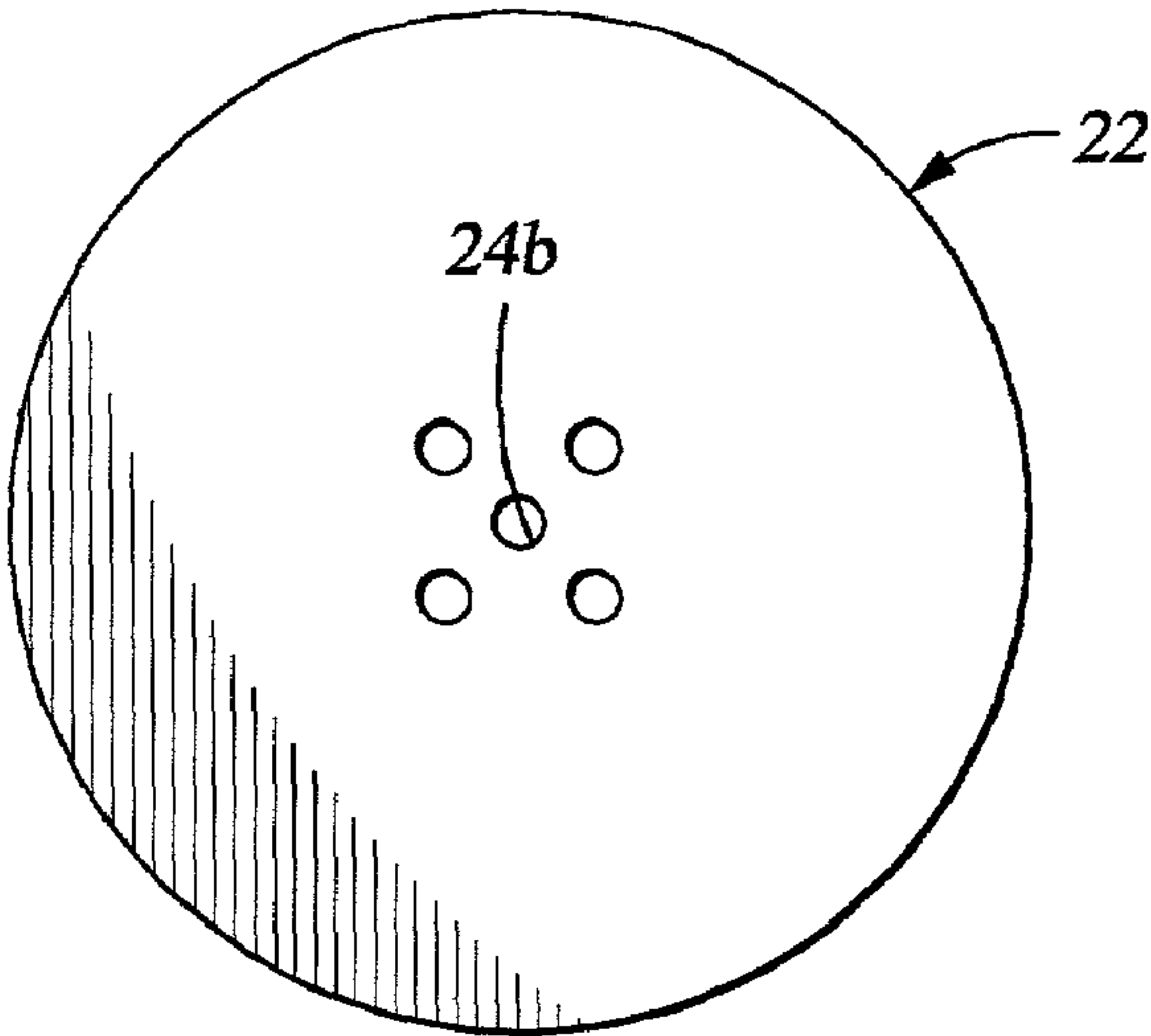
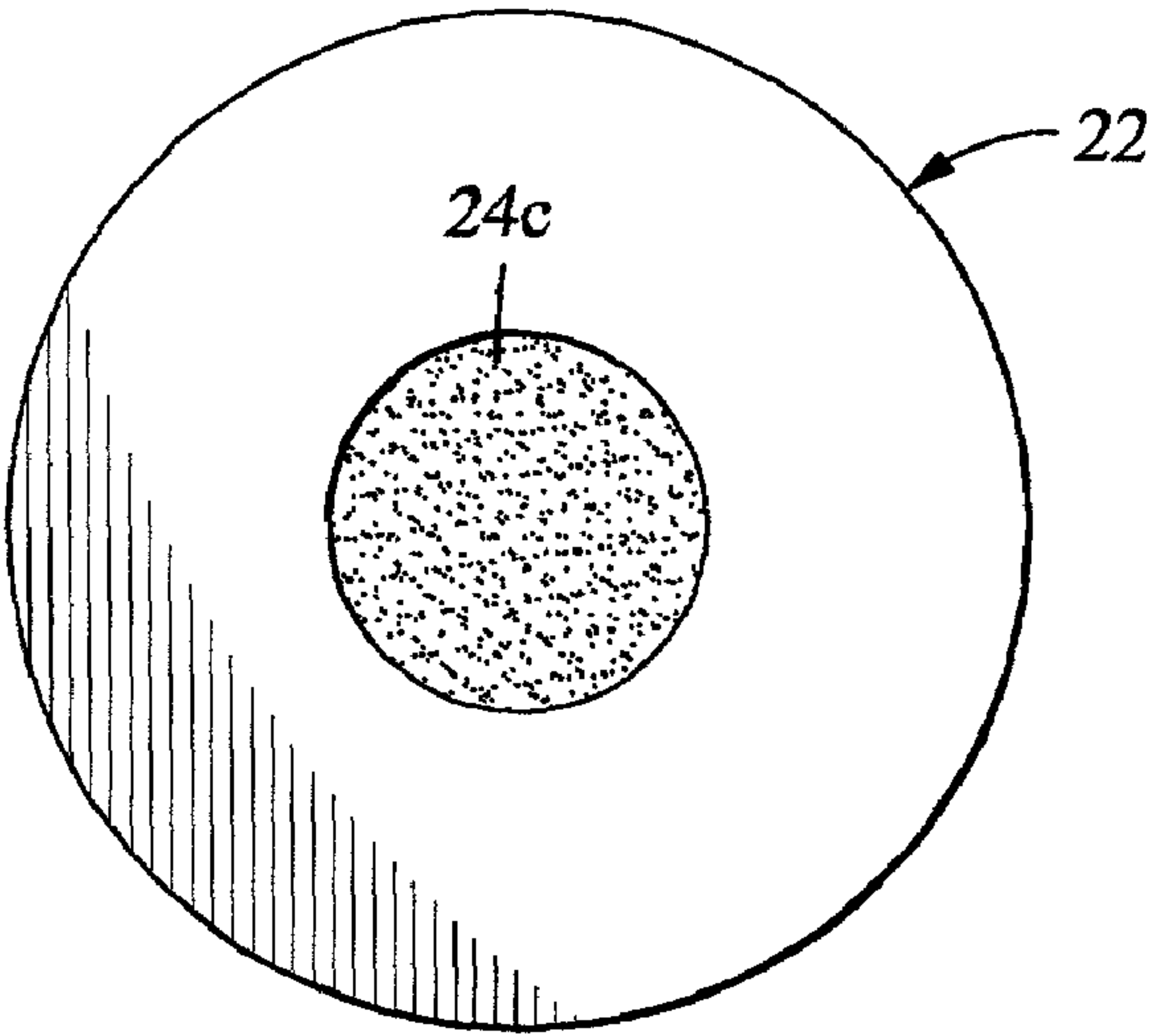


Fig. 6c



APPARATUS AND METHOD OF EVALUATING ELECTROPLATING SOLUTIONS AND CONDITIONS

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention generally relates to an apparatus and method of evaluating electroplating solutions and conditions.

[0003] 2. Description of the Related Art

[0004] Reliably producing sub-micron and smaller features is one of the key technologies for the next generation of very large scale integration (VLSI) and ultra large scale integration (ULSI) of semiconductor devices. However, as the fringes of circuit technology are pressed, the shrinking dimensions of interconnects in VLSI and ULSI technology have placed additional demands on the processing capabilities. The multilevel interconnects that lie at the heart of this technology require precise processing of high aspect ratio features, such as vias and other interconnects. Reliable formation of these interconnects is very important to VLSI and ULSI success and to the continued effort to increase circuit density and quality of individual substrates.

[0005] As circuit densities increase, the widths of vias, contacts and other features, as well as the dielectric materials between them, decrease to sub-micron dimensions, whereas the thickness of the dielectric layers remains substantially constant, with the result that the aspect ratios for the features, i.e., their height divided by width, increases. Many traditional deposition processes have difficulty filling sub-micron structures where the aspect ratio exceeds 2:1, and particularly where the aspect ratio exceeds 4:1. Therefore, there is a great amount of ongoing effort being directed at the formation of substantially void-free, sub-micron features having high aspect ratios.

[0006] Currently, copper and its alloys have become the metals of choice for submicron interconnect technology because copper has a lower resistivity than aluminum, ($1.7 \mu\Omega\text{-cm}$ compared to $3.1 \mu\Omega\text{-cm}$ for aluminum), and a higher current carrying capacity and significantly higher electromigration resistance. These characteristics are important for supporting the higher current densities experienced at high levels of integration and increased device speed. Further, copper has a good thermal conductivity and is available in a highly pure state.

[0007] Electroplating of conductive materials, such as copper, is one process being used to fill high aspect ratio features on substrates. Electroplating processes typically require a thin, electrically conductive seed layer to be deposited on the substrate. Electroplating is accomplished by applying an electrical current to the seed layer and exposing the substrate to an electrolytic solution containing metal ions which plate over the seed layer. The seed layer typically comprises a conductive metal, such as copper, and is conventionally deposited on the substrate using physical vapor deposition (PVD) or chemical vapor deposition (CVD) techniques. One problem in electroplating of conductive materials to fill a feature is that electroplated metal grows in all directions. Therefore, if near the mouth of a feature the rate of electroplating of the metal is high, a bridge may form over the mouth of the feature prior to complete

filling of the feature and thus may leave a void in the feature. The void may change the operating characteristics of the interconnect feature and may cause improper operation and premature breakdown of the device.

[0008] Superconformal or superfilling electrodeposition is one method of electroplating directed to filling features without the formation of voids. In superconformal electrodeposition at least one suppressor and at least one accelerator are added to the electroplating solution. It is believed that the suppressors inhibit electroplating of the substrate by striking a surface of the substrate and reducing the active surface area of the substrate available for the metal reduction process of electroplating. The suppressors are typically high molecular weight compounds, such as polyethers or other polymers. Since suppressors are typically used in dilute concentrations, it is believed that the transport of the suppressors to the surface of the substrate is a diffusion process. Under a diffusion process, the flux of the suppressors should be greater on the field areas and around the mouth of a feature rather than on the bottom of the feature. In comparison with the suppressors, molecules of the accelerators are much smaller and penetrate more easily to the bottom of the feature. For electroplating solutions having a superfill effect, the concentration ratio of accelerators-to-suppressors under electrolysis near the bottom of the feature increases leading to an increase in the metal deposition rate at the bottom of the feature or so-called "bottom-up" or superfill effect. As a consequence, electroplating occurs more rapidly on the bottom of a feature than on the field areas or on the edges of the mouth of a feature resulting in a "bottom-up" growth of the electroplated metal in the feature. Bottom-up growth reduces the likelihood of a formation of a bridge closing the mouth of a feature.

[0009] Typical electroplating solutions may comprise metal ions, pH adjusters, buffering salts, suppressors, accelerators, reducing agents, levelers, chelating agents, stabilizers, other electrolytes, and/or other additives. Typical suppressors include polyethers, such as polyethylene glycol, or other polymers, such as polypropylene, which act to inhibit the rate of electroplating. Typical accelerators include sulfides or disulfides, such as bis(3-sulfopropyl) disulfide, which are added to affect the microstructure of the electrodeposited metal. Because of the numerous possible compositions of an electroplating solutions, it may be difficult to predict the overall mechanism of an electroplating solution during electroplating. For example, for an electroplating solution containing suppressors and accelerators it is difficult to determine whether the electroplating solution will exhibit bottom-up growth at a particular electroplating parameter. Therefore, there is a need for a method and an apparatus for evaluating electroplating solutions.

[0010] A journal article entitled "Superconformal Electrodeposition of Copper in 500-900 nm Features," T. P. Moffat et al., *Journal of the Electrochemical Society*, 147 (12), p. 4524-4535 (2000) reports a study of electroplating solutions with and without suppressors and accelerators. The article reports that in the presence of suppressors and accelerators, the current-potential deposition reveals a wide hysteresis under direct and back potential scan, which does not take place in additive-free electroplating solutions. This hysteresis can indicate that the electroplating solution has the ability for superfill effect. However, this hysteresis response is inherent for electroplating solutions without

superfill ability as well. Therefore, this method cannot be used to estimate superfilling ability of an electroplating solution or to estimate the optimal electroplating conditions.

[0011] Therefore, there is a need for an improved apparatus and method of evaluating electroplating solutions and conditions

SUMMARY OF THE INVENTION

[0012] The present invention generally relates to an apparatus and method of evaluating electroplating solutions and conditions. In particular, the present invention relates to an apparatus and method of evaluating electroplating solutions containing additives, such as suppressors and accelerators.

[0013] In one embodiment, the method of evaluating electroplating solutions comprises utilizing an electrochemical measuring cell having a working electrode having a lid with at least one hole, a counter electrode, and a reference electrode. The working electrode, the counter electrode, and the reference electrode are immersed in at least one sample of at least one electroplating solution. The potential of the working electrode in the sample of the electroplating solution is measured over time with a constant current supplied to the working electrode. The electrochemical measurements may be used to determine which solutions are capable of bottom-up filling and may be used to estimate the optimal electroplating parameters.

[0014] In still another embodiment, the method of evaluating electroplating solutions comprises contacting an electrochemical measuring cell with an electroplating solution of an electroplating chamber. The electrochemical measuring cell comprises a working electrode, a counter electrode, and a reference electrode. Then, a potential of the working electrode is measured over time with a constant current supplied to the working electrode to provide a potential trace.

[0015] In one embodiment, the apparatus for evaluating electroplating solutions comprises a working electrode and a lid disposed over the working electrode. A chamber is formed between the working electrode and the lid. The lid further has at least one hole to allow an electroplating solution to flow into the chamber and reach the working electrode. In one aspect, the working electrode imitates the conditions occurring during electroplating in a feature.

[0016] In another embodiment, the apparatus for evaluating electroplating solutions, comprises a working electrode, a counter electrode, a reference electrode, a galvanostat coupled to the working electrode and the counter electrode to provide a constant current to the working electrode, and a voltmeter coupled between the working electrode and the reference electrode to measure the potential of the working electrode. The apparatus further comprises a lid disposed over the working electrode forming a chamber between the working electrode and the lid. The lid further has at least one hole to allow an electroplating solution to flow into the chamber and reach the working electrode.

[0017] In still another embodiment, the present invention relates to an apparatus for electroplating a substrate. The apparatus comprises a chamber body, an anode disposed in the chamber body, a contact ring disposed in the chamber body, one or more power supplies coupled to the anode and the contact ring, and an electrochemical measuring cell

having a working electrode, a counter electrode, and a reference electrode. In one aspect, the electrochemical measuring cell may be disposed in the chamber body. In another aspect, the electrochemical measuring cell may be coupled to an electrolyte output coupled to the chamber body.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] So that the manner in which the above recited features, advantages and objects of the present invention are attained and can be understood in detail, a more particular description of the invention, briefly summarized above, may be had by reference to the embodiments thereof which are illustrated in the appended drawings.

[0019] It is to be noted, however, that the appended drawings illustrate only typical embodiments of this invention and are therefore not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments.

[0020] FIG. 1 is a schematic cross-sectional view of one embodiment of an electrochemical measuring cell.

[0021] FIG. 2 is a schematic cross-sectional view of another embodiment of an electrochemical measuring cell.

[0022] FIG. 3 is a graph of traces of the potential of a working electrode over time of samples of an electroplating solution evaluated at different constant currents.

[0023] FIG. 4 is a graph of traces of the potential of a working electrode over time of samples of another electroplating solution evaluated at different constant currents.

[0024] FIG. 5 is a schematic cross-sectional view of one embodiment of an electrochemical measuring cell used in conjunction with one embodiment of an electroplating chamber.

[0025] FIGS. 6a-6c are bottom views of embodiments of a lid of a working electrode having at least one hole.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0026] FIG. 1 is a schematic cross-sectional view of one embodiment of an electrochemical measuring cell 10 useful in evaluating electroplating solutions. The cell 10 comprises a working electrode 12, a counter electrode 14, and a reference electrode 16 immersed in a solution 18. A galvanostat device 20 is coupled to the cell to control the current through the cell 10 at a preset value. A voltmeter 21 is coupled between the working electrode 12 and the reference electrode 16 to measure the potential of the working electrode 12.

[0027] A current is applied to the cell 10 so that the working electrode 12 acts as a cathode of the cell 10 and so that the counter electrode 14 acts as an anode of the cell 10. The reference electrode 16 is used as a reference point against which the potential of the working electrode 12 can be measured.

[0028] An example of a working electrode 12 is a copper wire electrode, a platinum rotating disk electrode, etc. An example of a counter electrode 14 is a copper electrode, a titanium electrode, a stainless steel electrode, etc. An example of a reference electrode 16 is a saturated calomel electrode, a hydrogen electrode, a silver/silver-chloride elec-

trode, a copper/copper sulfate electrode, or any other electrode assemblies that have an electrode potential independent of the electrolyte used in the cell 10.

[0029] The working electrode 12 is separated from the bulk solution 18a of the cell 10 by a lid 22. The lid 22 may be removable or may be integral to the working electrode 12. The lid 22 is shaped and sized so that there is a chamber 23 formed between the working electrode 12 and the lid 22. The lid 22 may be adjusted to adjust the size of the chamber 23. The lid 22 has at least one hole 24 which allows the solution 18 to flow through the hole 24 into the chamber 23 prior to reaching the working electrode 12. FIGS. 6a-6c, are bottom views of the lid 22 illustrating embodiments of the lid having at least one hole 24a. The lid may have a single hole as shown in FIG. 6a, the lid may have a plurality of holes 24b as shown in FIG. 6b, or the lid may have a plurality of holes comprising a porous membrane 24c as shown in FIG. 6c. The size of each hole is preferably small to imitate the mouth of a feature. The diameter of each hole is equal to or greater than the diameter of a mouth of a feature. In one embodiment, the total combined cross-sectional area of hole(s) 24 (whether a single hole, a plurality of holes, or a porous membrane) is equal to or less than about 30% of the exposed area 13 of the working electrode 12, preferably equal to or less than about 10% of the exposed area of the working electrode. In another embodiment, the total combined cross-sectional area of hole(s) 24 (whether a single hole, a plurality of holes, or a porous membrane) is equal to or less than about 0.8 mm^2 , preferably equal to or less than about 0.1 mm^2 .

[0030] The lid 22 may be adapted so that the chamber 23 is any volume, but the volume is preferably small to imitate the electroplating conditions occurring in a feature formed in the dielectric layer deposited over a semiconductor substrate. For example, the volume of the chamber 23 may be less than about 100 mm^3 .

[0031] In one embodiment, the at least one hole 24 may be formed at the side of the lid 22 (as shown in FIG. 2) in order to be positioned closer to the reference electrode 16 in order to more accurately measure the potential of the working electrode 12 by reducing the distance and, thus, the ohmic drop between the reference electrode 16 and the working electrode 12. In another embodiment, the working electrode 12 may be positioned adjacent the at least one hole 24 of the working electrode 12 in order to more accurately measure the potential at the working electrode 12 by reducing the distance and, thus, the ohmic drop between the reference electrode 16 and the working electrode 12. In still another embodiment, the distance between the working electrode 12 and the reference electrode 16 is kept constant between samples of electroplating solutions in order to increase the precision of the apparatus in evaluating different samples of electroplating solutions.

[0032] One embodiment of a method of evaluating electroplating solutions comprises measuring the potential of the working electrode 12 over time under a constant current supplied to the working electrode 12 by utilizing an electrochemical measuring cell, such as cell 10, containing the electroplating solution to be evaluated. In one embodiment, the bulk solution 18a is not agitated so that non-electrolytes in the electroplating solution, such as suppressors or accelerators, are limited to movement through the electroplating

solution by a diffusion process rather than a convection process. The method may comprise evaluating samples of the same electroplating solutions at different constant currents. The method may comprise evaluating samples of different electroplating solutions at the same constant current. The method may further comprise evaluating samples of the electroplating solutions at different temperatures.

[0033] For example, an electroplating solution containing 0.3 M of copper sulfate (CuSO_4), about 10% by weight of sulfuric acid (H_2SO_4), about 60 ppm of chloride ion, 15 ml/L of the suppressor polyoxypropylene-polyoxyethylene copolymer, and 5 ml/L of the accelerator mercapto-propane-sulfonate, was evaluated in an electrochemical measuring cell, such as cell 10 with a working electrode 12, a counter electrode 14, and a reference electrode 16. The at least one hole 24 of the lid 22 on the working electrode 12 comprised a single hole having a diameter between about 0.1 mm and about 0.2 mm and the volume of the chamber 23 of the lid 22 was between about 60 mm^3 and about 80 mm^3 . Samples of the electroplating solution were evaluated at about room temperature. The working electrode 12, the counter electrode 14, and the reference electrode 16 were placed in the cell 10 and were immersed in the electroplating solution. The potential of the working electrode 12 over time under constant current supplied to the working electrode by a galvanostat device 20 was measured.

[0034] FIG. 3 is a graph of traces of the potential of the working electrode 12 over time of samples of the electroplating solution evaluated at different constant currents. Potential of the working electrode in volts is graphed on the y-axis and time in seconds is graphed on the x-axis. Trace 30 is of a sample of the electroplating solution at a constant current of about 5 mA/cm^2 through the working electrode 12. Trace 31 is of another sample of the electroplating solution at a constant current of about 10 mA/cm^2 through the working electrode 12. Trace 32 is of another sample of the electroplating solution at a constant current of about 15 mA/cm^2 through the working electrode 12. Trace 33 is of another sample of the electroplating solution at a constant current of about 25 mA/cm^2 through the working electrode. Both trace 31 and trace 32 show a relative minimum 34 in which the slope of the traces becomes positive. Trace 30 and trace 33 do not show a relative minimum. It has been observed by scanning electron microscope photographs of semiconductor substrates electroplated with this electroplating solution at room temperature that at current densities at the cathode of about 10 mA/cm^2 and about 15 mA/cm^2 bottom-up growth occurs while at current densities of about 5 mA/cm^2 and 20 mA/cm^2 bottom-up growth does not occur.

[0035] Not wishing to be bound by any one theory, it is believed that the amount of additives and other components of electroplating solutions in the chamber 23 are decreasing faster than the amount of additives and other components of the electroplating solution entering the chamber 23. The amount of additives in the chamber 23 may be decreasing as a result of leaving the chamber, being broken down under the current, and/or being consumed in the electroplated film. The depletion rates of suppressors and accelerators are different. To provide superfill effect, the suppressors must deplete faster than the accelerators. When the surface concentration ratio of accelerators-to-suppressors become such that the accelerators start to dominate in chamber 23, a potential trace of the working electrode at constant current

exhibits a relative minimum on the negative potential trace. The relative minimum indicates that electroplating now proceeds at the working electrode **12** more easily. The greater the positive slope (dE/dt) of the negative potential trace indicates that the electroplating conditions may occur more readily at the working electrode **12**.

[0036] It is believed that the mechanism of an electroplating solution occurring at the lid of the working electrode is similar to the mechanism occurring at a feature of a substrate. Therefore, a potential trace which exhibits a relative minimum indicates an electroplating solution which at that current density is capable of bottom-up filling in a feature of a substrate because the relative minimum indicates neutralization of the suppressor's action under these electroplating conditions. On the other hand, a potential trace which does not exhibit a relative minimum indicates an electroplating solution which at that current density bottom-up filling in feature of a substrate does not occur because the concentration changes of all the components of the electroplating solution, including accelerators and suppressors, do not increase the ability and ease of electroplating. Furthermore, the slope of the traces can be used to determine the relative rates of bottom-up filling occurring in a feature of a substrate.

[0037] In addition, the time interval of when the relative minimum occurs in the potential trace can be used to estimate a time when bottom-up filling occurs in a feature of a substrate. The time interval ΔT_w of the working electrode from the beginning of electrolysis to the relative minimum is proportional to the transition time ΔT_f of a feature of a substrate required for bottom-up electroplating to begin. The transition time ΔT_f of a feature must be shorter than that of the working electrode because the diffusion flow of the components of the electroplating solution into the feature comes through a opening which has an area that is smaller than the inner surface area of the feature where electrodeposition proceeds. On the other hand, the working electrode is flat and, hence, the area of the diffusion flow and the area of the electrode surface are the same. The transition time ΔT_f of a feature is approximated to be proportional to the time interval ΔT_w of the working electrode by a factor of the flow of electroplating solution per the inner surface area of the feature as shown in Equation #1 below.

$$\Delta T_f = (S_o/S)_f \Delta T_w \text{tm Equation 1:}$$

[0038] wherein $(S_o)_f$ stands for the surface area of the opening or mouth of a feature which approximates the flow of bulk electroplating solution through the mouth of the feature, and $(S)_f$ stands for the plateable inner surface area of the feature.

[0039] Equation 1 can be used to estimate the transition time ΔT_f of a feature of a substrate required for bottom-up electroplating to begin. For example, for a feature having a circular mouth having a diameter of about $0.2 \mu\text{m}$ and a height of about $1.0 \mu\text{m}$, the surface area of the mouth $(S_o)_f$ of the feature would be $\pi(0.2/2)^2 = 0.0314 \mu\text{m}^2$ and the surface area of the feature $(S)_f$ would be equal to the area of the walls plus the area of the bottom of the feature which is equal to $\pi(0.2 \mu\text{m})(1.0 \mu\text{m}) + 0.0314 \mu\text{m}^2 = 0.660 \mu\text{m}^2$. Therefore, $(S_o/S)_f$ is equal to about $1/21$ ($0.0314/0.660$). For trace **31**, as shown in **FIG. 3**, which has a relative minimum at about 115 seconds, bottom-up filling is estimated to begin in the feature in about 5.5 seconds ($1/21 \times 115$ seconds).

[0040] **FIG. 4** is a graph of the traces of the potential of the working electrode **12** over time of samples of another electroplating solution evaluated at different constant currents. The electroplating solution contained about 0.3 M of copper sulfate (CuSO_4), about 10% by weight of sulfuric acid (H_2SO_4), and about 60 ppm of chloride ion. The electroplating solution was evaluated in an electrochemical measuring cell, such as cell **10** with a working electrode **12**, a counter electrode **14**, and a reference electrode **16**. The diameter of the hole **24** of the lid **22** on the working electrode **12** was between about 0.1 mm and about 0.2 mm and the volume of the chamber **23** of the lid **22** was between about 60 mm^3 and 80 mm^3 . The solution was evaluated at about room temperature. Trace **40** is a sample of the electroplating solution at a constant current of 5 mA/cm^2 through the working electrode **12**. Trace **41** is a sample of the electroplating solution at a constant current of 10 mA/cm^2 through the working electrode **12**. Trace **42** is a sample of the electroplating solution at a constant current of 15 mA/cm^2 through the working electrode **12**. Trace **43** is a sample of the electroplating solution at a constant current of 25 mA/cm^2 through the working electrode. Traces **40-44** do not show a relative minimum. Thus, this electroplating solution under these current densities at about room temperature do not exhibit bottom-up filling.

[0041] Thus, the present apparatus and method may be used to screen electroplating solutions to determine which electroplating solutions exhibit bottom-up filling at a certain current density at a certain temperature. Furthermore, the transition time for when bottom-up filling of a feature of a substrate begins to occur can be estimated. In addition, the relative rates of bottom-up filling may be compared between samples of electroplating solutions. Thus, electroplating parameters, such as concentrations of the electroplating solution, current density, temperature, and time, may be optimized.

[0042] In one embodiment, the electrochemical measuring cell may be used separately apart from an electroplating chamber to optimize electroplating conditions. In another embodiment, the electrochemical measuring cell may be used in conjunction with an electroplating chamber to optimize electroplating conditions.

[0043] **FIG. 5** is a schematic cross-sectional view of one embodiment of the electrochemical measuring cell **110** used in conjunction with one embodiment of an electroplating chamber **50**, known as a fountain plater. The electrochemical measuring cell **110** comprises a working electrode **112**, a counter electrode **114**, and a reference electrode **116** adapted to contact the electroplating solution. A galvanostat device **120** is coupled to the cell to control the current through the cell **110** at a preset value. A voltmeter **121** is coupled between the working electrode **112** and the reference electrode **116** to measure the potential of the working electrode **112**.

[0044] The working electrode **112** is separated from the bulk electroplating solution by a lid **122**. The lid **122** may be removable or may be integral to the working electrode **112**. The lid **122** is shaped and sized so that there is a chamber **123** formed between the working electrode **112** and the lid **122**. The lid **122** may be adjusted to adjust the size of the chamber **123**. The lid **122** has at least one hole **124** which allows the solution **118** to flow through the hole **124** into the

chamber 123 prior to reaching the working electrode 112. The lid 122 may have a single hole, the lid may have a plurality of holes, or the lid may have a plurality of holes comprising a porous membrane. The size of each hole is preferably small to imitate the mouth of a feature. The diameter of each hole is equal to or greater than the diameter of a mouth of a feature. In one embodiment, the total combined cross-sectional area of hole(s) 124 (whether a single hole, a plurality of holes, or a porous membrane) is equal to or less than about 30% of the exposed area 113 of the working electrode 112, preferably equal to or less than about 10% of the area of the working electrode. In another embodiment, the total combined cross-sectional area of hole(s) 24 (whether a single hole, a plurality of holes, or a porous membrane) is equal to or less than about 0.8 mm², preferably equal to or less than about 0.1 mm². The lid 122 may be adapted so that the chamber 123 is any volume, but the volume is preferably small to imitate the electroplating conditions occurring in a feature formed in the dielectric layer deposited over a semiconductor substrate. For example, the volume of the chamber 123 may be less than about 100 mm³.

[0045] The electroplating chamber 50 may include a top opening 52 and a movable substrate support 54 adapted to be positioned through the top opening 52 to support a substrate 56 in an electroplating solution. A contact ring 60 is configured to secure and support a substrate 56 in position during electroplating, and permits the electroplating solution contained in the electroplating chamber 50 to contact the surface 55 of the substrate 56 while it is immersed in an electroplating solution. A negative pole of a power supply 64 is connected to a plurality of contacts 62 of the contact ring 60 which are typically mounted about the periphery of the substrate 56 to provide multiple circuit pathways to the substrate 56. An anode assembly 58 may be disposed near a bottom portion of the electroplating chamber 50. The anode assembly 58 is coupled to a positive pole of the power supply 64.

[0046] An electroplating solution is supplied to a cavity 68 or chamber body defined within the electroplating chamber 50 via electrolyte input port 70 from electrolyte input supply 72. The electrolyte supply 72 may provide an electroplating solution comprising inhibitors, accelerators, metal ions, pH adjustors, buffering salts, reducing agents, levelers, chelating agents, stabilizers, other electrolytes, other additives, or combinations thereof. During electroplating, the electroplating solution is supplied to the cavity 68 so that the electroplating solution overflows from a lip 69 into an annular drain 76. The annular drain 76 drains into electrolyte output port 78 which discharges to electrolyte output 80. In one embodiment, the electrolyte output 80 may be connected to the electrolyte input supply 72 to provide a closed loop for the electroplating solution contained within the electroplating chamber 50, such that the electroplating solution may be recirculated in the electroplating chamber 50. The motion associated with the recirculation of the electroplating solution also assists in transporting the electroplating solution from the anode assembly 58 to the surface 55 of the substrate 56. In one embodiment, the electrolyte input supply 72 may act as a regeneration element in which the electroplating solution is replenished, refreshed, or replaced with a chemical solution which may comprise inhibitors, accelerators, metal ions, pH adjustors, buffering salts, reducing agents,

levelers, chelating agents, stabilizers, other electrolytes, other additives, or combinations thereof.

[0047] The substrate 56 is positioned within an upper portion 54 of the cell 50, such that the electroplating solution flows along the surface 55 of the substrate 56 during operation. A negative charge applied from the negative pole of the power supply 64 via the contacts 62 to a seed layer deposited on plating surface 55 of substrate 56 in effect makes the substrate a cathode. The metal ions may be added to the electroplating solution and/or may be supplied by a consumable anode assembly. The seed layer formed on the surface 55 of the substrate 56 attracts metal ions carried by the electroplating solution to electroplate a metal on a surface 55 of a substrate 56. The anode assembly 58 may optionally further include a permeable membrane 88 covering the anode assembly 58 to prevent the contamination of the substrate 56 from anode sludge produced by a consumable anode.

[0048] The electrochemical measuring cell 110 may be positioned anywhere inside the cavity 68 of the electroplating chamber 50 as long as the electrochemical measuring cell is in contact with the electroplating solution. For example, as shown in FIG. 5, the electrochemical measuring cell 110 may be positioned in area 90. For example, the electrochemical measuring cell 110 may also be positioned in area 94. In one aspect, the electrochemical measuring cell 110 is positioned in the chamber body outside a flow of the electroplating solution from the anode assembly 58 to the contact ring 60 in order to prevent disrupting the flow of electroplating solution to the substrate 56 and causing non-uniformity in the electroplating of the substrate 56. For example, the electrochemical measuring cell 110 may be positioned in area 90.

[0049] The electrochemical measuring cell 110 may also be coupled to the electrolyte output 80. For example, the electrochemical measuring cell 110 may be positioned anywhere between the annular drain 76 and the electrolyte input port 70. For example, the electrochemical measuring cell 110 may be positioned at area 98. The electrochemical measuring cell 110 may be positioned prior or after the electrolyte input supply 72.

[0050] The electrochemical measuring cell 110 may be coupled to a controller 99 which directs the electrochemical measuring cell 110 in monitoring and evaluating the electroplating solution. For example, the electrochemical cell 110 may be coupled to the controller 99 through the galvanostat 120 and the voltmeter 121. The controller 99 may also be coupled to the electrolyte input supply 72 to direct the electrolyte input supply 72 to add a chemical solution to the cavity 68 of the electroplating chamber 50 in order to replenish, refresh, or replace the electroplating solution of the electroplating chamber 50 based upon the measurements of the electrochemical measuring cell 110.

[0051] In one embodiment, the electrochemical measuring cell 110 may monitor or evaluate the electroplating solution in situ while a substrate is being electroplated in the electroplating chamber 50. Alternatively, the electrochemical measuring cell 110 may monitor or evaluate the electroplating solution before or after a substrate is electroplated. In addition, the electrochemical measuring cell 110 may compare electroplating conditions of an electroplating solution used to electroplate one substrate from another.

[0052] In one embodiment, the electrochemical measuring cell **110** may monitor and evaluate an electroplating solution by measuring the potential of the working electrode **12** over time at a certain constant current to provide a potential trace. The potential trace may be analyzed to determine the electroplating conditions that will result from an electroplating solution. The potential trace may be compared with other potential traces to determine the electroplating conditions that will result from an electroplating solution. For example, if the slopes of the potential traces from an electroplating solution used to electroplate one substrate from an electroplating solution used to electroplate another substrate (of course, this may be the same electroplating solution used to electroplate both substrates in which the composition of the electroplating solution has changed over time) change, then this may show that the rate of bottom-up filling is changing. In another example, if a potential trace of a certain electroplating used to process one or more substrates no longer shows a minimum, this may signal that the electroplating solution is no longer capable of bottom-up growth. In another example, if a potential trace of a certain electroplating solution used to process one or more substrates shows a longer and longer time period in where the minimum occurs, this may indicate that the electroplating solution is less effective in providing bottom-up growth. As a consequence, the electrolyte input supply **72** may add a chemical solution to the electroplating chamber to refresh, replenish, or replace the electroplating solution used based upon the evaluation from the electrochemical measuring cell **110**.

[0053] While the foregoing is directed to embodiments of the present invention, other and further embodiments of the invention may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

1. Method of evaluating an electroplating solution, comprising:

immersing a working electrode, a counter electrode, and a reference electrode in a sample of an electroplating solution;

measuring a potential of the working electrode in the sample of the electroplating solution over time with a constant current supplied to the working electrode; and

identifying whether the electroplating solution is capable of obtaining bottom-up growth at the constant current in a feature of a substrate.

2. The method of claim 1, wherein identifying whether the electroplating solution is capable of obtaining bottom-up growth at the constant current in a feature of a substrate comprises determining whether the potential of the working electrode over time exhibits a relative minimum at the constant current.

3. The method of claim 2, further comprising estimating a time to initiate bottom-up growth in the feature from the relative minimum.

4. The method of claim 1, wherein the electroplating solution comprises inhibitors and accelerators.

5. The method of claim 1, wherein measuring the potential of the working electrode comprises utilizing a lid disposed over the working electrode, the lid forming a chamber between the working electrode and the lid, and the lid having at least one hole formed therethrough.

6. The method of claim 5, wherein the chamber has a volume of less than about 100 mm^2 and the at least one hole has a total combined cross-sectional area equal to or less than about 30% of an exposed area of the working electrode.

7. Method of evaluating an electroplating solution, comprising:

immersing a working electrode, a counter electrode, and a reference electrode in a sample of an electroplating solution;

measuring a potential of the working electrode in the sample of the electroplating solution over time with a constant current supplied to the working electrode; and

determining whether the potential of the working electrode over time exhibits a relative minimum at the constant current.

8. The method of claim 7, wherein the electroplating solution comprises inhibitors and accelerators.

9. The method of claim 7, wherein measuring the potential of the working electrode comprises utilizing a lid disposed over the working electrode, the lid forming a chamber between the working electrode and the lid, and the lid having at least one hole formed therethrough.

10. The method of claim 9, wherein the chamber has a volume of less than about 100 mm^2 and the at least one hole has a total combined cross-sectional area equal to or less than about 30% of an exposed area of the working electrode.

11. Method of evaluating an electroplating solution, comprising:

immersing a working electrode, a counter electrode, and a reference electrode in a sample of an electroplating solution, the electroplating solution comprising inhibitors and accelerators;

measuring a potential of the working electrode in the sample of the electroplating solution over time with a constant current supplied to the working electrode by utilizing a lid disposed over the working electrode, the lid forming a chamber between the working electrode and the lid, the lid having at least one hole formed therethrough, the chamber having a volume of less than about 100 mm^2 and the at least one hole having a total combined cross-sectional area equal to or less than about 30% of an exposed area of the working electrode; and

determining whether the potential of the working electrode over time exhibits a relative minimum at the constant current.

12. Method of evaluating an electroplating solution, comprising:

performing a plurality of trials, each trial comprising:

immersing a working electrode, a counter electrode, and a reference electrode in a sample of an electroplating solution;

measuring a potential of the working electrode in the sample of the electroplating solution over time with a constant current supplied to the working electrode; and

identifying whether the electroplating solution is capable of obtaining bottom-up growth at the constant current in a feature of a substrate.

13. The method of claim 12, wherein performing a plurality of trials comprises evaluating a plurality of electroplating solutions at the same constant current.

14. The method of claim 12, wherein performing a plurality of trials comprises evaluating one electroplating solution at a plurality of constant currents.

15. The method of claim 12, wherein performing a plurality of trials comprises evaluating a plurality of electroplating solutions at a plurality of constant currents.

16. The method of claim 12, wherein performing a plurality of trials comprises evaluating at least one electroplating solution at one or more constant currents at a plurality of temperatures.

17. The method of claim 12, wherein identifying whether the electroplating solution is capable of obtaining bottom-up growth at the constant current in a feature of a substrate comprises determining whether the potential of the working electrode over time exhibits a relative minimum at the constant current.

18. The method of claim 17, further comprising estimating a time to initiate bottom-up growth in the feature from the relative minimum.

19. The method of claim 17, further comprising comparing the slopes of the potentials of the trials which exhibit a relative minimum to determine a relative rate of bottom-up growth.

20. The method of claim 12, wherein the electroplating solution comprises inhibitors and accelerators.

21. Apparatus for evaluating electroplating solutions, comprising:

a working electrode;

a lid disposed over the working electrode and forming a chamber between the working electrode and the lid, the lid having at least one hole formed therethrough;

a counter electrode;

a reference electrode;

a galvanostat coupled to the working electrode and the counter electrode; and

a voltmeter coupled to the working electrode and the reference electrode.

22. The apparatus of claim 21, wherein the lid has a bottom wall and a sidewall, the at least one hole being disposed in the bottom wall.

23. The apparatus of claim 21, wherein the lid has a bottom wall and a sidewall, the at least one hole being disposed in the sidewall.

24. The apparatus of claim 21, wherein the lid is removable.

25. The apparatus of claim 21, wherein the at least one hole has a total combined cross-sectional area equal to or less than about 30% of an exposed area of the working electrode.

26. The apparatus of claim 21, wherein the at least one hole has a total combined cross-sectional area equal to or less than about 10% of an exposed area of the working electrode.

27. The apparatus of claim 21, wherein the at least one hole has a total combined cross-sectional area equal to or less than about 0.8 mm².

28. The apparatus of claim 21, wherein the at least one hole has a total combined cross-sectional area equal to or less than about 0.1 mm².

29. The apparatus of claim 21, wherein the chamber has a volume of less than about 100 mm³.

30. The apparatus of claim 21, wherein the at least one hole comprises a single hole.

31. The apparatus of claim 21, wherein the at least one hole comprises a plurality of holes.

32. The apparatus of claim 21, wherein the at least one hole comprises a porous membrane.

33. Apparatus for evaluating electroplating solutions, comprising:

a working electrode;

a lid disposed over the working electrode, the lid comprising at least one hole; and

a chamber formed between the working electrode and the lid.

34. The apparatus of claim 33, wherein the lid has a bottom wall and a sidewall, the at least one hole being disposed in the bottom wall.

35. The apparatus of claim 33, wherein the lid has a bottom wall and a sidewall, the at least one hole being disposed in the sidewall.

36. The apparatus of claim 33, wherein the lid is removable.

37. The apparatus of claim 33, wherein the at least one hole has a total combined cross-sectional area equal to or less than about 30% of an exposed area of the working electrode.

38. The apparatus of claim 33, wherein the at least one hole has a total combined cross-sectional area equal to or less than about 10% of an exposed area of the working electrode.

39. The apparatus of claim 33, wherein the at least one hole has a total combined cross-sectional area equal to or less than about 0.8 mm².

40. The apparatus of claim 33, wherein the at least one hole has a total combined cross-sectional area equal to or less than about 0.1 mm².

41. The apparatus of claim 33, wherein the chamber has a volume of less than about 100 mm³.

42. The apparatus of claim 33, wherein the at least one hole comprises a single hole.

43. The apparatus of claim 33, wherein the at least one hole comprises a plurality of holes.

44. The apparatus of claim 33, wherein the at least one hole comprises a porous membrane.

45. An apparatus for electroplating a substrate; comprising:

a chamber body;

an anode disposed in the chamber body;

a contact ring disposed in the chamber body;

one or more power supplies coupled to the anode and the contact ring; and

an electrochemical measuring cell having a working electrode, a counter electrode, and a reference electrode.

46. The apparatus of claim 45, wherein the electrochemical measuring cell is disposed in the chamber body.

47. The apparatus of claim 46, wherein the electrochemical measuring cell is disposed in the chamber body outside a flow of electroplating solution from the anode to the contact ring.

48. The apparatus of claim 45, further comprising an electrolyte output coupled to the chamber body, the electrochemical measuring cell being coupled to the electrolyte output.

49. The apparatus of claim 45, further comprising:

an electrolyte input supply coupled to the chamber body; and

a controller coupled to the electrochemical measuring cell and the electrolyte input supply.

50. The apparatus of claim 49, wherein the controller is adapted to control the electrolyte input supply to add a chemical solution to the chamber body.

51. The apparatus of claim 50, wherein the electrolyte input supply is a regeneration element adapted to recirculate electroplating solution to the chamber body.

52. The apparatus of claim 45, further including a galvanostat coupled to the working electrode and the counter electrode of the electrochemical measuring cell and a voltmeter coupled to the working electrode and the reference electrode of the electrochemical measuring cell.

53. The apparatus of claim 45, wherein the electrochemical measuring cell has a lid disposed over the working electrode and forming a chamber between the working electrode and the lid, the lid having at least one hole formed therethrough.

54. The apparatus of claim 53, wherein the at least one hole has a total combined cross-sectional area equal to or less than about 30% of an exposed area of the working electrode.

55. The apparatus of claim 53, wherein the at least one hole has a total combined cross-sectional area equal to or less than about 10% of an exposed area of the working electrode.

56. The apparatus of claim 53, wherein the at least one hole has a total combined cross-sectional area equal to or less than about 0.8 mm^2 .

57. The apparatus of claim 53, wherein the at least one hole has a total combined cross-sectional area equal to or less than about 0.1 mm^2 .

58. The apparatus of claim 53, wherein the chamber has a volume of less than about 100 mm^3 .

59. The apparatus of claim 53, wherein the at least one hole comprises a single hole.

60. The apparatus of claim 53, wherein the at least one hole comprises a plurality of holes.

61. The apparatus of claim 53, wherein the at least one hole comprises a porous membrane.

62. An apparatus for electroplating a substrate; comprising:

a chamber body;

an anode disposed in the chamber body;

a contact ring disposed in the chamber body;

one or more power supplies coupled to the anode and the contact ring; and

an electrochemical measuring cell having a working electrode, a counter electrode, a reference electrode, and a lid disposed over the working electrode,

wherein the lid forms a chamber between the working electrode and the lid, and the lid has at least one hole having a total combined cross-sectional area equal to or less than about 30% of an exposed area of the working electrode formed therethrough.

63. The apparatus of claim 62, wherein the at least one hole has a total combined cross-sectional area equal to or less than about 10% of an exposed area of the working electrode.

64. The apparatus of claim 62, wherein the chamber has a volume of less than about 100 mm^3 .

65. The apparatus of claim 62, wherein the at least one hole comprises a single hole.

66. The apparatus of claim 62, wherein the at least one hole comprises a plurality of holes.

67. The apparatus of claim 62, wherein the at least one hole comprises a porous membrane.

68. An apparatus for electroplating a substrate; comprising:

a chamber body;

an anode disposed in the chamber body;

a contact ring disposed in the chamber body;

one or more power supplies coupled to the anode and the contact ring;

an electrolyte input supply coupled to the chamber body,

an electrochemical measuring cell having a working electrode, a counter electrode, and a reference electrode, and

a controller coupled to the electrochemical measuring cell and the electrolyte input supply.

69. The apparatus of claim 68, wherein the controller is adapted to control the electrolyte input supply to add a chemical solution to the chamber body.

70. The apparatus of claim 69, wherein the electrolyte input supply is a regeneration element adapted to recirculate electroplating solution to the chamber body.

71. A method of evaluating an electroplating solution, comprising:

contacting an electrochemical measuring cell with an electroplating solution of an electroplating chamber, the electrochemical measuring cell comprising a working electrode, a counter electrode, and a reference electrode; and

measuring a potential of the working electrode over time with a constant current supplied to the working electrode to provide a potential trace.

72. The method of claim 71, wherein contacting the electrochemical measuring cell with the electroplating solution comprises disposing the electrochemical measuring cell within a chamber body of the electroplating chamber.

73. The method of claim 71, wherein contacting the electrochemical measuring cell with the electroplating solution comprises coupling the electrochemical measuring cell to an electrolyte output of the electroplating chamber.

74. The method of claim 71, further comprising evaluating the potential trace.

75. The method of claim 74, wherein evaluating the potential trace comprises determining whether the potential trace exhibits a relative minimum.

76. The method of claim 75, wherein evaluating the potential trace further comprises determining a time interval when the relative minimum occurs.

77. The method of claim 74, wherein evaluating the potential trace comprises evaluating the slope of the potential trace.

78. The method of claim 74, wherein evaluating the potential trace comprises comparing the potential to at least one other potential trace.

79. The method of claim 71, further comprising adding a chemical solution to the electroplating chamber based upon the potential trace.

80. The method of claim 79, wherein adding the chemical solution to the electroplating chamber is automatically performed by a controller coupled to the electrochemical measuring cell.

81. The method of claim 71, wherein the electroplating solution comprises inhibitors and accelerators.

82. A method of evaluating an electroplating solution, comprising:

contacting an electrochemical measuring cell with an electroplating solution of an electroplating chamber, the electrochemical measuring cell comprising a working electrode, a counter electrode, and a reference electrode;

measuring a potential of the working electrode over time with a constant current supplied to the working electrode to provide a potential trace; and

and adding a chemical solution to the electroplating chamber based upon the potential trace.

83. The method of claim **82**, wherein adding the chemical solution to the electroplating chamber is automatically performed by a controller coupled to the electrochemical measuring cell.

84. The method of claim **82**, wherein the electroplating solution comprises inhibitors and accelerators.

* * * * *