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(54) METHOD AND APPARATUS FOR ELECTROPOLISHING

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(57) **ABSTRACT**

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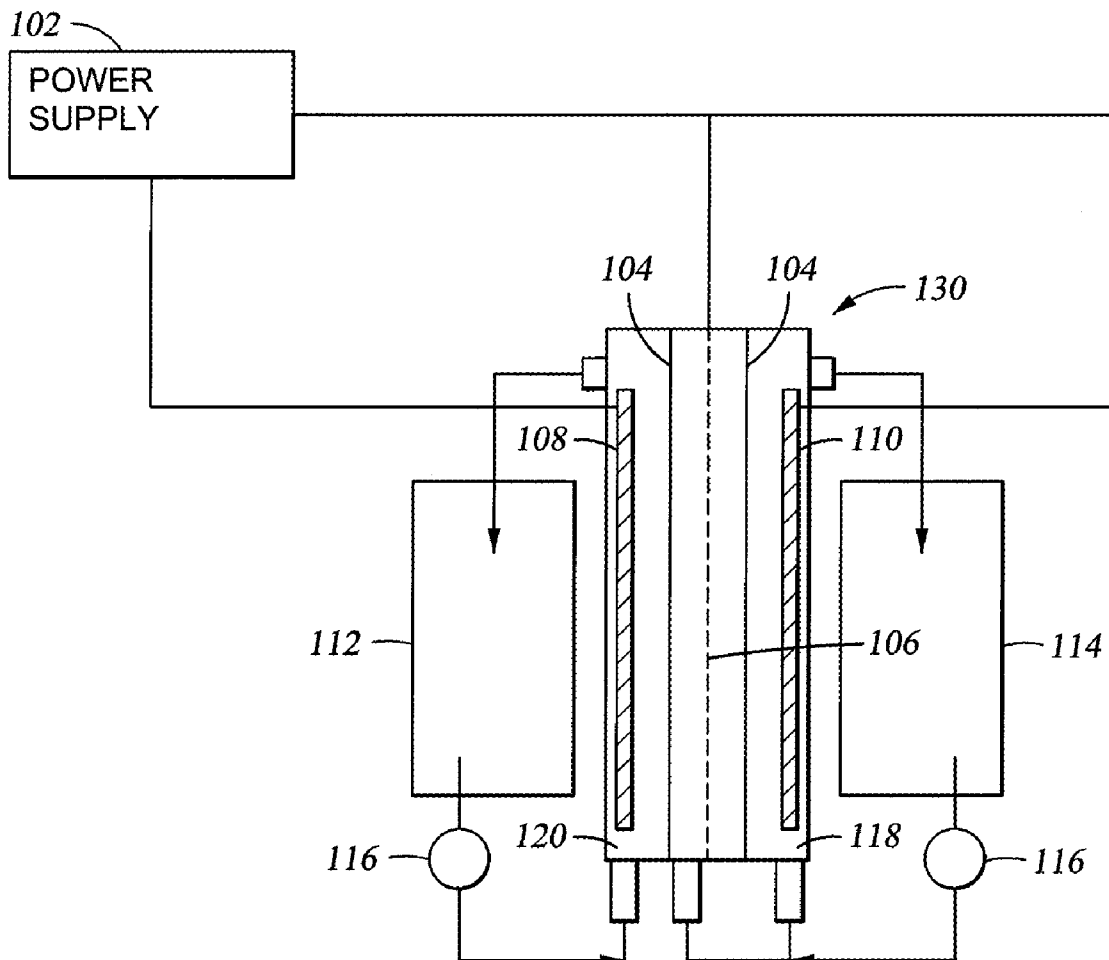
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Related U.S. Application Data

(60) Provisional application No. 60/726,933, filed on Oct. 14, 2005.

The present invention generally includes deposition and electropolishing methods and an apparatus comprising an electroplating cell and auxiliary cell. In one embodiment for electropolishing a substrate, a cycle is performed in which the substrate is alternately placed in an anolyte solution to remove material and a catholyte solution to deposit material. As the cycle is repeated successively, an exposed layer disposed on the substrate is planarized. In another embodiment, an auxiliary cell may be used to deposit the ultrathin seed layer prior to electroplating.



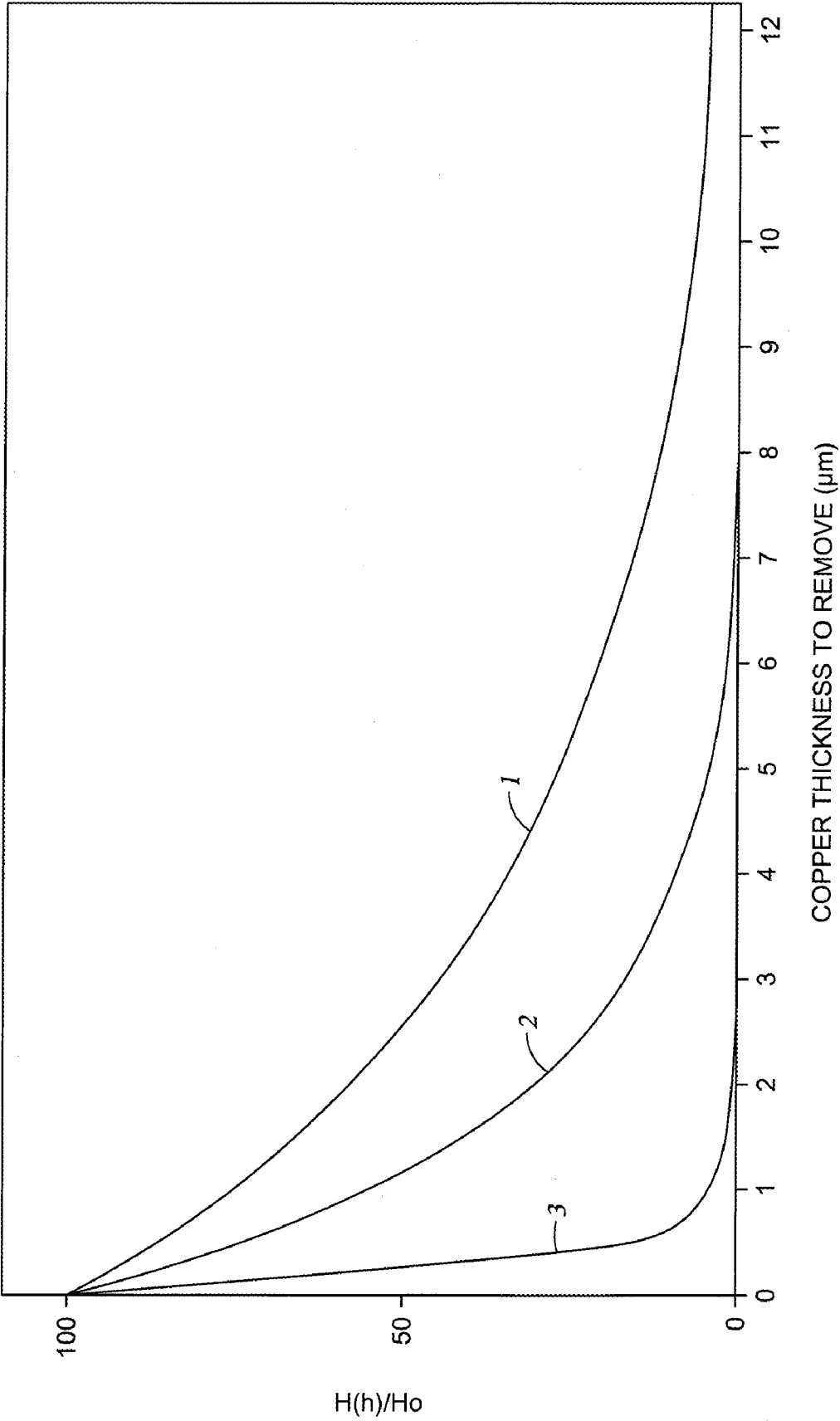


Fig. 1

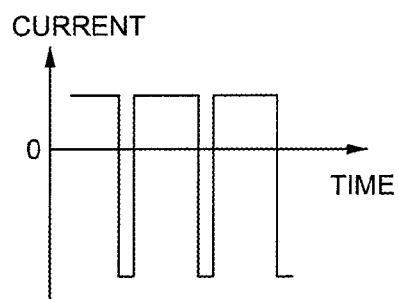


Fig. 2A

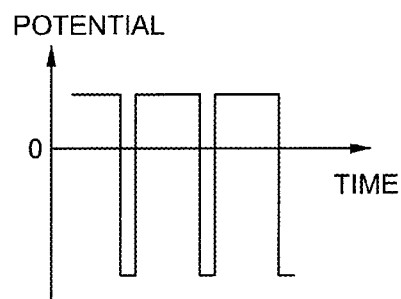


Fig. 2C

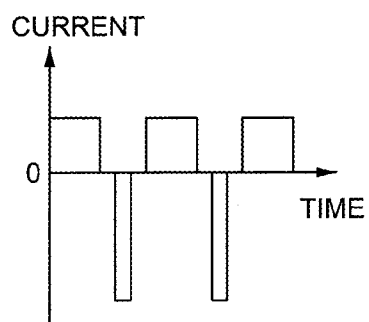


Fig. 2B

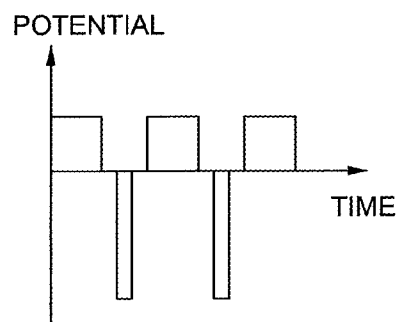


Fig. 2D

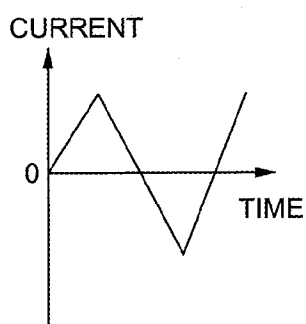


Fig. 2E

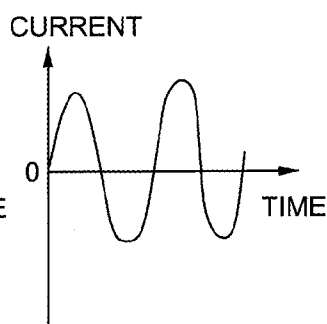


Fig. 2F

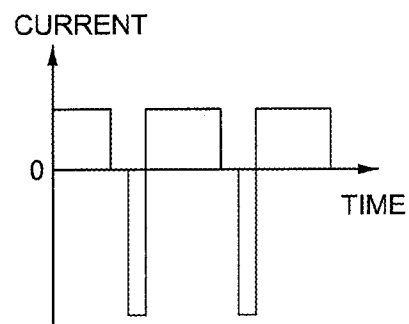


Fig. 2G

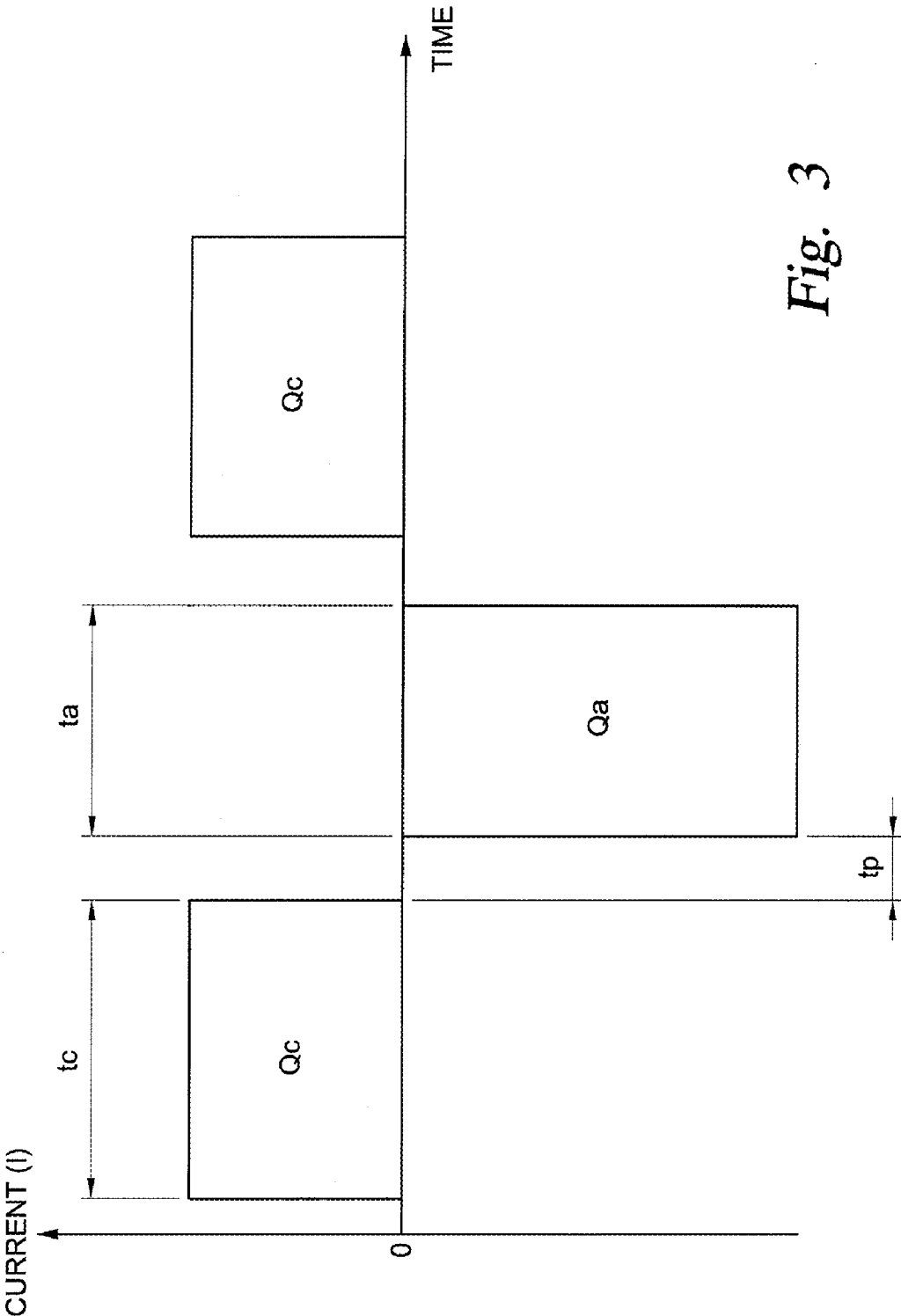


Fig. 3

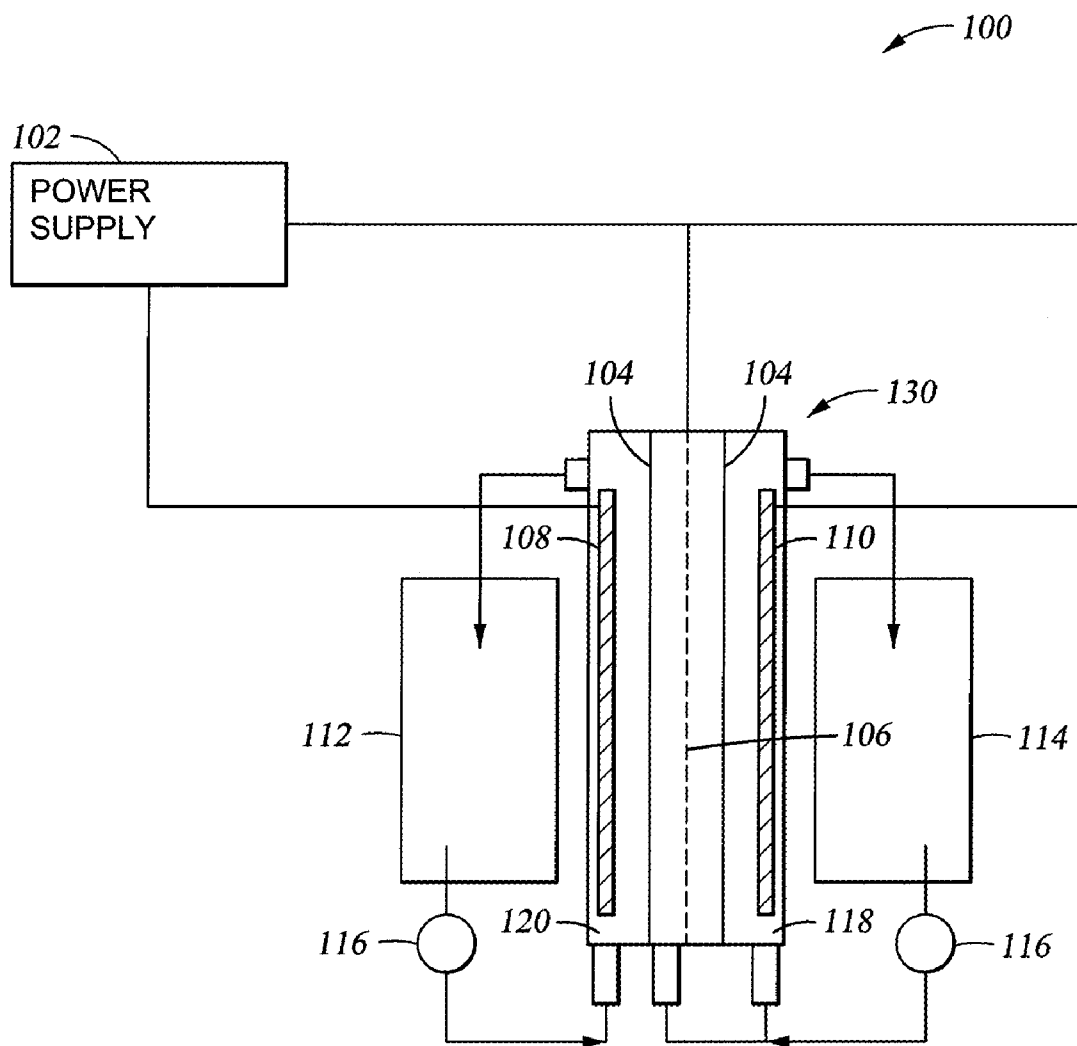


Fig. 4

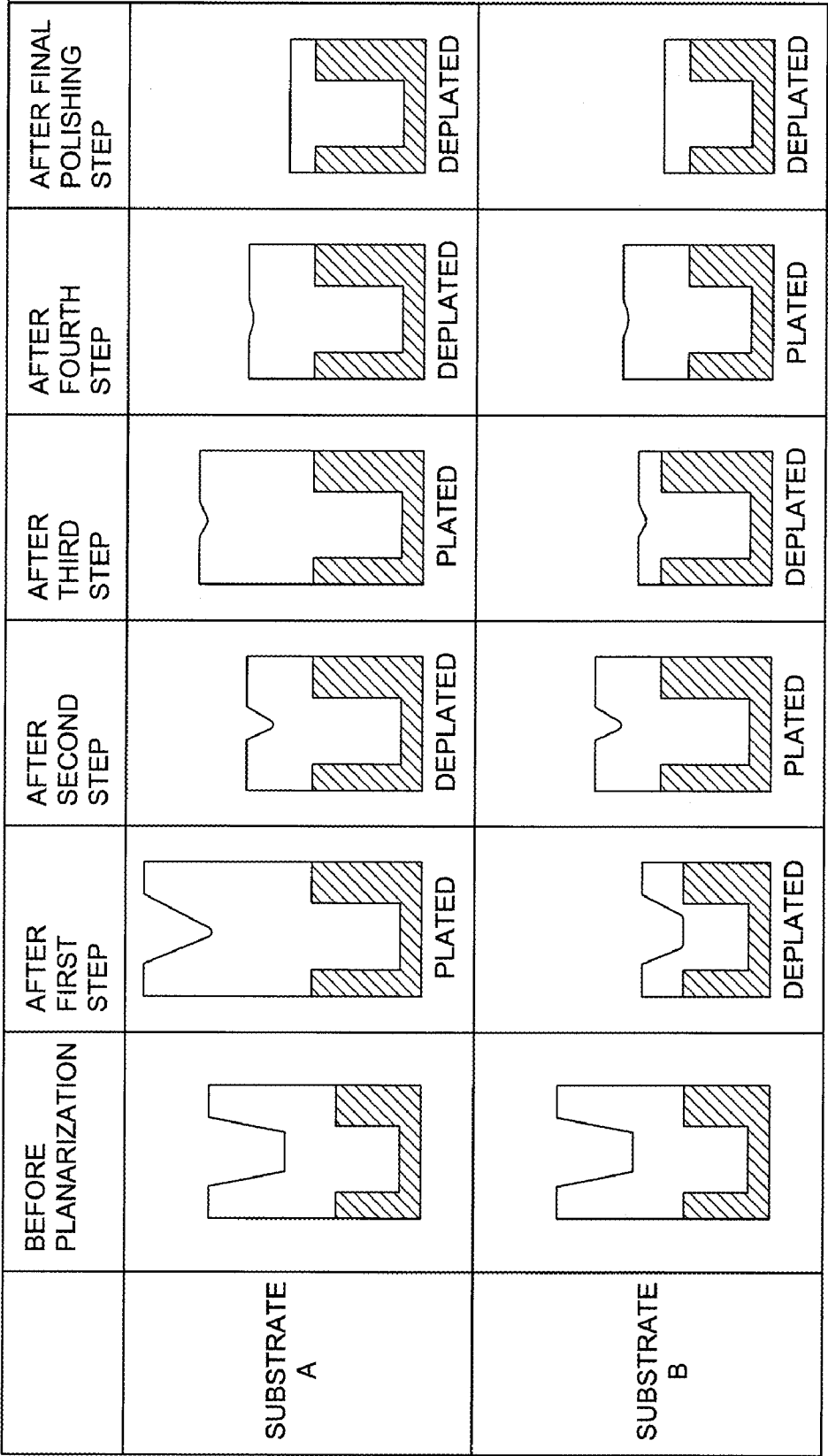


Fig. 5

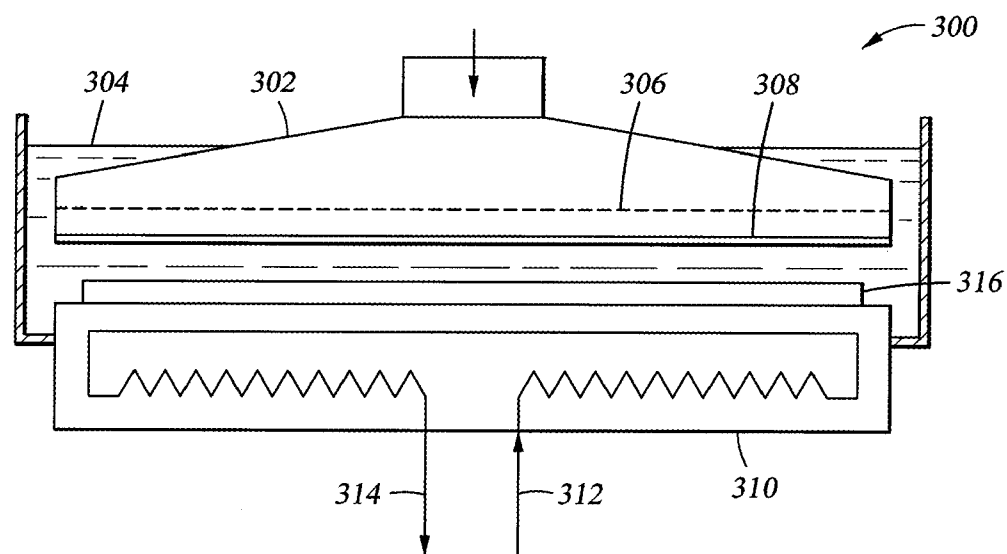


Fig. 6

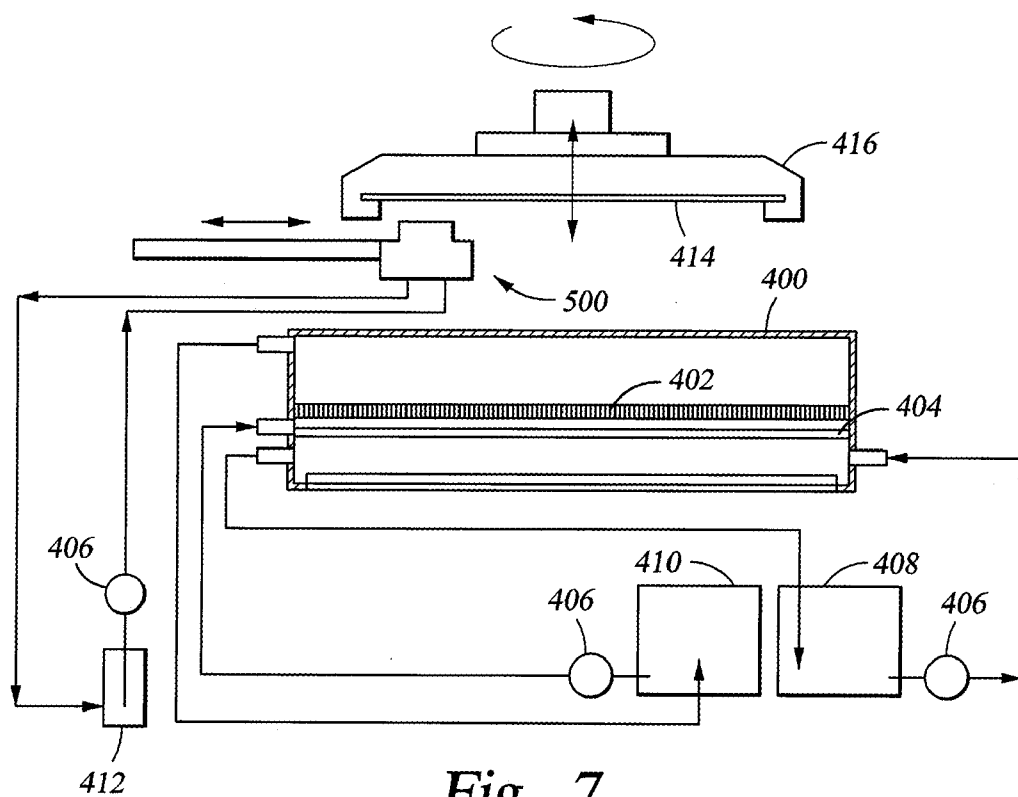


Fig. 7

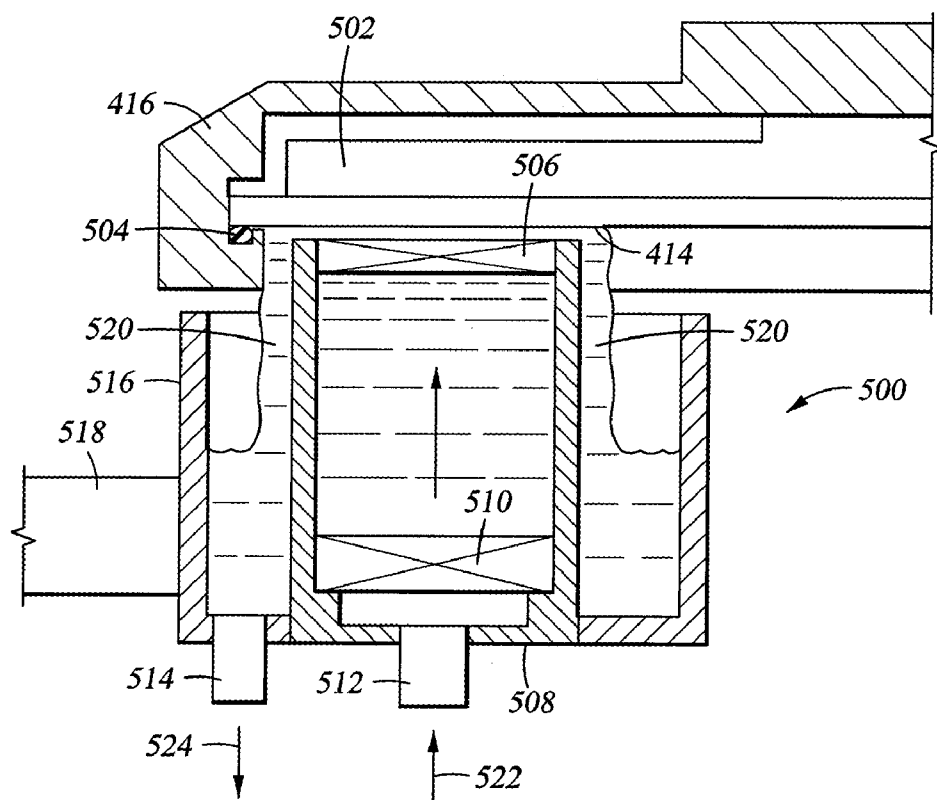


Fig. 8

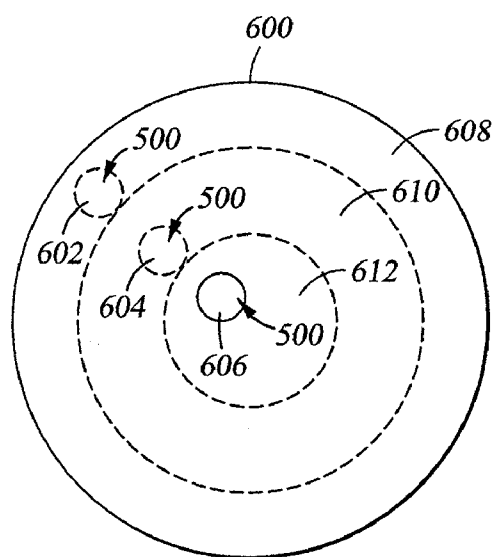


Fig. 9A

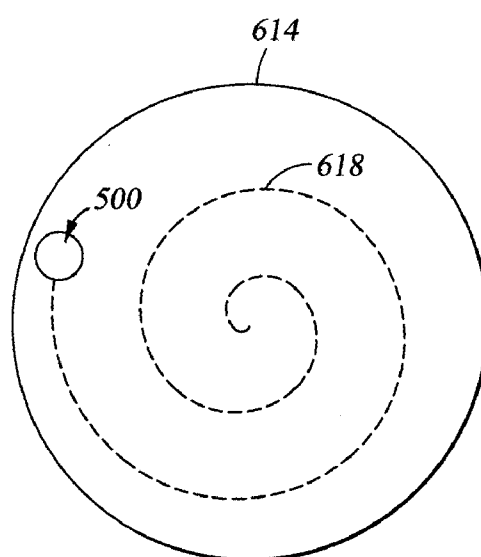


Fig. 9B

METHOD AND APPARATUS FOR ELECTROPOLISHING

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application Ser. No. 60/726,933 (APPM/010637L), filed Oct. 14, 2005, which is hereby incorporated by reference.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] Embodiments of the present invention generally relate to an electropolishing process and an auxiliary cell for wafer and contact ring electrochemical treatment.

[0004] 2. Description of the Related Art

[0005] Reliably producing sub-half 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 limits of circuit technology are pushed, the shrinking dimensions of interconnects in VLSI and ULSI technology have placed additional demands on the processing capabilities. Reliable formation of these interconnects is important to VLSI and ULSI success and to the continued effort to increase circuit density and quality of individual substrates and die.

[0006] Interconnects and multilevel interconnect layers are generally formed by use of two major process steps. The two steps are: 1) a material deposition step, such as a physical vapor deposition (PVD) step and/or electrochemical plating (ECP) step, and then 2) a material removal step, such as a chemical mechanical polishing (CMP) step or an electrochemical mechanical polishing (ECMP) step. During the PVD and/or ECP deposition steps, narrow and wide surface features of varying height are often generated across the substrate surface, which need to be planarized before the next interconnect layer is formed over the current layer. The term planarized, or planarization, as used herein is intended to describe the act of reducing the topographical variation in height of the surface features on the top surface of the substrate. A more planarized surface, or higher degree of planarization, is intended to describe a state when there are less topographical variations on the substrate surface (e.g., the surface is flatter). To compensate for these topographic variations it is common to deposit more material than is necessary to fill the interconnect features, commonly called "overburden", to assure that the surface can be fully planarized by use of a CMP or ECMP process after the material deposition step. The substrate throughput through the interconnect forming sequence is greatly affected by the amount of overburden, since it affects the amount of time it takes to deposit the extra material and then remove the extra material.

[0007] Typically, the surface topography of a substrate will vary depending on the density or size of features formed thereon. The variation in topography can make the process of achieving a planar surface difficult using CMP techniques. For example, in conventional CMP techniques, the removal rate of copper material overlying a dense feature area of the substrate surface is slower than the removal rate

of copper material overlying a comparatively less dense feature area of the substrate. The relatively uneven removal rates can result in underpolishing of areas of the substrate, leaving residual copper material on the substrate after the polishing process. The presence of residual material on a substrate can detrimentally affect subsequent processing and result in reduced device yields and reduced substrate throughput.

[0008] Electropolishing removes conductive materials, such as copper, from a substrate surface by electrochemical dissolution with minimal or no polishing pressures. Electrochemical dissolution is typically performed by applying an anodic bias to the substrate and removing material by an ion dissolution mechanism without the need of mechanical abrasion.

[0009] Electropolishing of copper has conventionally been performed under potential static conditions, (i.e., a constant potential is applied between an electrode and the substrate. However, such a method requires a sophisticated power supply that can maintain a constant potential between the substrate and the electrode by using a feedback mechanism. One difficulty with this method is that the electrode condition has to be constantly monitored to control the potential accurately and reliably for effective polishing.

[0010] Further, conventional electropolishing techniques have difficulty planarizing a substrate surface. For example, a non-planar surface can result from protuberances, or peaks, formed over dense features, and recesses, or valleys, formed over wide features. The electropolishing technique may remove the material from the protuberances and recesses at approximately the same rate. Therefore, the same non-planarity as was present before the electropolishing technique was performed may be maintained. The amount of material that can be removed by the electropolishing technique to avoid dishing or other topographical defects compared to the amount of material disposed above the recesses may be limited. For example, conventional electropolishing processes generally cannot planarize surfaces that have relatively deep and wide surface features (e.g., 10-200 μm in width). Additional polishing techniques may still be required as described above, which may not satisfactorily polish the material above the dense and wide features, such as retaining residue material on the substrate surface.

[0011] Therefore, there is a need for an apparatus and method for planarizing a metal layer on a substrate that leaves less topographic variations prior to performing CMP or ECMP processes.

SUMMARY OF THE INVENTION

[0012] The present invention generally includes deposition and electropolishing methods and an apparatus comprising an electroplating cell and auxiliary cell. In one embodiment, a method for electropolishing includes cyclically processing a substrate to planarize an exposed conductive layer and detecting an endpoint of the planarization process. The cyclical planarization process includes exposing the conductive layer to a catholyte solution of a first chemistry and exposing the conductive layer to an anolyte solution of a second chemistry.

[0013] In another embodiment for electropolishing a substrate, a cycle is performed in which the substrate is alter-

nately placed in an anolyte solution to remove material on the substrate and a catholyte solution to deposit material on the substrate. As the cycle is repeated successively, an exposed layer disposed on the substrate is planarized. In another embodiment, an auxiliary cell may be used to deposit the ultrathin seed layer prior to electropolishing.

[0014] In another embodiment, a method for electropolishing is disclosed. The method comprises providing a first and a second substrate, wherein each substrate has a layer deposited thereon, performing a first sequence of exposing the first substrate to a catholyte solution of a first chemistry, exposing the second substrate to an anolyte solution of a second chemistry, providing a current density to both the catholyte solution and the anolyte solution, performing a second sequence of exposing the first substrate to an anolyte solution of the second chemistry, exposing the second substrate to a catholyte solution of the first chemistry, providing a second current density to both the catholyte solution and the anolyte solution, and repeating at least one of the first and second sequences. The current density to the catholyte and anolyte solutions may be the same or different. The first and second current densities may also be the same or different.

[0015] In another embodiment, a method for electropolishing is disclosed. The method comprises providing a substrate on a substrate chuck within an electropolishing cell, wherein the substrate has a layer deposited thereon, providing an electrolyte within the electropolishing cell, wherein the electrolyte is in contact with the substrate, cooling the substrate through the substrate chuck to a temperature below or about the freezing point of the electrolyte, and electropolishing the layer deposited on the substrate.

[0016] In another embodiment, a method for electropolishing is disclosed. The method comprises reverse current electropolishing in an electrolyte composition having effective leveling agents and a high concentration of copper salt. The reverse current electrolysis uses substantially the same quantity of electricity during the cathodic (i.e., plating) period and the anodic (i.e., deplating) period. Thus, material is redistributed along the surface more uniformly to achieve a surface planarization.

[0017] In another embodiment, a method of depositing is disclosed. The method comprises providing at least one auxiliary cell. Each auxiliary cell comprises an arm and a chamber connected to the arm. The auxiliary cell is moved across a surface of the substrate or the contact ring to deposit or remove material.

[0018] In another embodiment, an apparatus is disclosed. The apparatus comprises an auxiliary cell coupled to a robotic arm. The auxiliary cell comprises a chamber connected to the arm. The arm has a range of motion to allow the auxiliary cell to be moved across a surface of the substrate during operation.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] So that the manner in which the above recited features of the present invention can be understood in detail, a more particular description of the invention, briefly summarized above, may be had by reference to embodiments, some of which are illustrated in the appended drawings. It is

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

[0020] FIG. 1 is a graph showing the topographical variation versus the amount of material that needs to be removed.

[0021] FIGS. 2A-2D illustrate various square-wave alternating cathodic-anodic potential pulses that may be used to perform an electropolishing process in accordance with embodiments described herein.

[0022] FIGS. 2E-2G illustrate various shaped cathodic-anodic potential pulses that may be used to perform an electropolishing process in accordance with the embodiments described herein.

[0023] FIG. 3 illustrates the features of a single cathodic-anodic potential pulse.

[0024] FIG. 4 is a schematic representation of one embodiment of an electropolishing cell.

[0025] FIG. 5 is a chart showing two wafers as they proceed through the electropolishing process of the present invention.

[0026] FIG. 6 is a schematic representation of another embodiment of an electropolishing cell having a cooled susceptor.

[0027] FIG. 7 is a schematic representation of an electropolishing cell having an auxiliary cell.

[0028] FIG. 8 is a schematic representation of the auxiliary cell of FIG. 7.

[0029] FIGS. 9A and 9B are schematic representations of the auxiliary cell across the substrate surface.

[0030] To facilitate understanding, identical reference numerals have been used, where possible, to designate identical elements that are common to the figures. It is contemplated that elements disclosed in one embodiment may be beneficially utilized on other embodiments without specific recitation.

DETAILED DESCRIPTION

[0031] The present invention comprises a method and apparatus for depositing and electropolishing a substrate. One processing system that may be adapted to benefit from the present invention is the SLIMCELL® ECP system, available from Applied Materials, Inc., located in Santa Clara, Calif. It is contemplated that other processing systems, including those from other manufacturers, may be adapted to practice the invention.

Single Chamber Design

[0032] Conventional chemical mechanical polishing (CMP) processes used to planarize the overburden of copper formed on the substrate surface are generally based on a rotating polishing pad that touches the surface of the substrate. For processes that include fragile low-k dielectrics materials, it is important to find a way to remove copper so that the low-k material will not be damaged due to the force exerted by pad against the surface of the substrate. ECMP methods that apply less contact force, use electrochemical methods that utilize the surface contact to activate and

expose the protruding surfaces while the copper in the recessed portions of the top surface is protected from electrolytic dissolution by inhibitors contained in the polishing electrolyte. Still it is desirable that the planarization method not contact the substrate surface in an effort to prevent harm to the dielectric layer, or generate surface defects (e.g., scratches).

[0033] Achieving good electropolishing results when the geometry of the substrate surface contains narrow and wide undulation, or surface features, often caused by the various features formed beneath the deposited layer(s), is a challenge. In typical applications the peak-to-valley topographical undulation on the surface can reach 0.6 micrometers (μm) in height and be about 200 μm in width. These types of surface features that are challenging to planarize, especially because the typical overburden on substrates are generally between about 0.5 and about 1.2 μm thick. To get a relatively well planarized surface with this complicated geometry, the smoothing power, or ability to improve the peak-to-peak surface topography, using a “no mechanical contact” electropolishing process has to be at least 10-20 times better than the current state-of-the-art electropolishing processes used today. Typically, the most difficult surface topography to planarize is a relatively deep and wide surface features (more than 10-20 μm in width).

[0034] FIG. 1 is a graph of topographical variation versus the amount of material that needs to be removed to achieve a planar surface using a typical electropolishing process for various sized features. Referring to FIG. 1, the curves 1, 2 and 3 illustrate the percentage change in topographical variation for small sized features (i.e., period of undulation <2 μm wide), medium sized features (i.e., period of undulation is between 2 μm and about 10 μm) and wide features (i.e., period of undulation is between 20 μm and about 200 μm), respectively. The percentage of topographic variation, which is plotted on the Y-axis, the height of the maximum peak to valley variation (i.e., $H(h)$) on the substrate at any given time divided by the initial maximum peak to valley variation (i.e., H_0). Referring to FIG. 1, to planarize small features using a typical electropolishing process (curve 1), one needs to remove about 1 μm of the copper layer. To planarize medium size features (curve 2) and wide features (curve 3) about 6 μm and about >12 μm of copper, respectively, must be removed using a typical electropolishing process in order to achieve the same degree of planarity as the small features plotted in curve 1. Typically, the maximum overburden on the substrate surface is only 1 μm , so typical electropolishing processes will not achieve a high degree of planarity for medium or wide features, because there is not enough overburden on the substrate surface to achieve a completely planar surface. One will also note that there is no “theoretical restrictions” on the ability to achieve a completely planarized surface for even medium and wide features, if the initial copper layer is thick enough.

[0035] In one embodiment, a novel electropolishing process, or process sequence, has been created by the inventors that achieves planarity independent of the initial overburden layer thickness on the filed region. In one aspect, instead of performing an electropolishing process that uses only anodic dissolution of overburden layer to planarize the surface, the novel electropolishing process uses a combination of copper electrochemical dissolution and also a copper electrodeposition process. The chemical composition of the electropol-

ishing electrolyte and the plating conditions (e.g., the applied bias (current or voltage), substrate rotation speed, electrolyte flow rate) are selected so that the surface planarization is relatively fast and takes place both under cathodic and anodic processes. Using the embodiments described herein, it is possible to planarize the copper surface without changing the average copper layer thickness.

[0036] In one aspect, the applied bias (current or voltage) is pulse type wave form that has cathodic and anodic aspect. FIGS. 2A-2G illustrate some waveforms that may be used to perform the electropolishing process. In one aspect, the duration of cathodic pulse (element t_c) and anodic pulse (element t_a) both vary from about 1 second to about 1000 seconds. In one aspect, it may be desirable to add a pause between positive and negative pulses of a duration (t_p), which may be between about 0 and about 5 seconds.

[0037] The electropolishing method described herein does not require the “leveling power” of the electrolyte under cathodic (or “plating”) periods nor under anodic (or “deplating”) periods of this electrochemical process to be inordinately high to achieve a desired planarity. The term leveling power is generally defined as the ability to reduce the planarity of a surface per unit of time or thickness (e.g., $(H(h)-H_0)/H_0$) over a period time).

[0038] Using the processes described herein the planarization of any size feature will proceed even when the “total” leveling effect (or the sum of “cathodic” or “anodic” leveling) is positive and also when viewing each process separately one of these components (cathodic or anodic) is not enhancing the planarity or the substrate surface, or exhibiting a leveling effect. In general, a positive leveling effect means that during plating or deplating the coefficient k in Wagner’s equation (i.e., $H=H_0 \exp(-kH_0h/a)$) is positive, however the coefficient k can also be negative or close to zero. When $k=0$, the planarization becomes zero. When k is negative, one will see the increase in the surface feature’s amplitude instead of planarization. The constant k will vary based on various electrochemical factors, such as types of chemistry, current density, etc.

[0039] In one aspect of the electropolishing process, the electropolishing process consists of two electrochemical processing steps: 1.) an electrochemical deposition step of material (e.g., copper) on the substrate using a bath that has a high leveling power, and 2.) removing at least a portion of the added layer in the same, or a different, electropolishing bath that has a high electropolishing (i.e., leveling) ability. The amount of additional material that needs to be deposited to achieve a planarized surface depends on the size of the surface features (e.g., height and width) that need to be planarized, and the “leveling power” of the electrolyte(s) used to cause the planarization process.

[0040] The electropolishing process generally includes the sequence of repetitively completing an electrochemical deposition step and an electropolishing step until the surface of the substrate is planarized. In one aspect of the invention, filling the device features and the electropolishing process are separated. The separation allows the early stages of the feature filling process to be performed in any manner to assure that the planarization steps will not affect device performance or device yield.

[0041] The electrochemical deposition step generally includes the step of electrochemically depositing a layer on

the surface of the substrate. In one aspect, the electrochemical deposition step may be performed in the same chamber and electrolyte bath. In another aspect, the electrochemical deposition step may be performed in the same chamber, but using a different electrolyte bath that has improved leveling power due to the addition of various organic additives to the electrolyte, such as a levelers. In another aspect, the electrochemical deposition step may be performed in a different chamber and using an electrolyte that has an improved leveling power due to the addition of various organic additives to the bath, such as a levelers.

[0042] The electropolishing step generally includes the step of electropolishing a layer from the surface of the substrate. In one aspect, the electropolishing step may be performed in the same chamber and electrolyte bath. In another aspect, the electropolishing step may be performed in the same chamber, but using a different electrolyte. In this case the composition of the bath may be changed to improve the anodic leveling power of the bath. In one aspect, the electropolishing step uses a bath containing about 85 wt. % H_3PO_4 , H_3PO_4/H_2SO_4 , or $H_4P_2O_7$ to electropolish a metal layer containing copper. In another aspect of the electropolishing step, the electropolishing process may be performed in a different chamber using a different electrolyte. In this case the electrolyte can be configured to have an improved anodic leveling power. Examples of exemplary electrolytes and electropolishing cells that may be adapted to perform aspects of the invention disclosed herein are further described in the commonly assigned U.S. Pat. Nos. 6,723, 224, 6,908,540, 6,951,599, and US Patent Application Publication No. 2003-0209523 A1, which are all incorporated by reference herein in their entireties.

[0043] It should be noted that the steps in the electropolishing process may be performed many more times than illustrated here (e.g., 10 times, 100 times, 1,000 times) to provide a desired level of planarization.

[0044] In one aspect, it may be desirable to avoid an electropolishing process that requires the use of two different electrolyte chemistries to perform the electroless process, due to the increase in system complexity and the need to control two different chemistries. Therefore, in one aspect, a single electrolyte bath is used to perform both the deposition and the anodic deplating process. In one embodiment, the single electrolyte bath contains a copper salt (e.g., $CuSO_4$, $Cu_2P_2O_7$, $Cu(BF)_4$, etc.) and cathodic leveling additives. In another aspect, the single electrolyte bath contains a copper salt (e.g., $CuSO_4$, $Cu_2P_2O_7$, $Cu(BF)_4$, etc.) that is added into a standard electropolishing solution (e.g., 85 wt. % H_3PO_4 , H_3PO_4/H_2SO_4 , $H_4P_2O_7$, etc.). In another embodiment, a copper plating bath is used that has a high leveling power, for example, a copper sulfate superfill bath (e.g., conventional Enthone or Rohm & Haas additives (accelerator and suppressor)) and a copper sulfate leveling bath with E-Brite or UBAC additives. In both these embodiments, the substrate biasing parameters (e.g., cathodic pulse width (t_c), anodic pulse width (t_a) resting time period (t_r), magnitude of the cathodic pulse (i_c or V_c), and magnitude of the anodic pulse (i_a or V_a)) are selected to increase the total leveling effect of the planarization process to achieve the highest leveling power. In one embodiment, it may be desirable to find an electrolyte composition that combine high leveling power, high polishing performance and meets

the specified requirements for the final copper surface (e.g., brightness, uniformity, low defect count, etc.).

[0045] According to the electroplating theory, the comparison of current traces obtained at low rotation speeds (i.e., rpm) and high rotation speeds shows qualitatively the plating/deplating current difference between recesses (low rpm) and tips (high rpm) of the substrate's surface profile. It should be noted that a drop in current density during plating or an increase in current density during deplating at higher substrate rotation speeds, is an indicator of increased planarization of the surface.

TABLE I

Features	Initial Height H_0 (Angstroms)	Height after electroplanarization H (Angstroms)	Planarization effect $H_0 - H/H_0$ (percent)
Array 100 micron trench - 100 micron space	5300	3200	40
Array 50 micron trench - 50 micron space	5280	1600	70
Array 90 micron trench - 90 micron space	3000	800	79
Array 10 micron trench - 10 micron space	1000	50	95
Prototruding spot 1200 microns in width	31000	16000	50
Array 0.18 micron trench - 0.18 micron space	2200	<50	>96
Array 1 micron trench - 100 micron space	2800	<50	>96

[0046] Table I illustrates an example of process results for the planarization of different sized features by the method described herein. The test substrate with 1.2 μm thick copper layer has been electrochemically planarized to remove 0.3 μm of copper so that the final copper thickness was 0.9 μm . As follows from Table I, in spite of the very thin layer removed, the planarization effect for features up to 100 μm in width is comparable with that of conventional CMP processes.

[0047] The processing time of planarization methods described herein may be longer than conventional CMP or ECMP methods, if the thickness of the fluid dynamic boundary layer is not optimized. In one case, the fluid dynamic boundary layer is formed by rotating the substrate at a rotation speed of about 10 to about 100 rpm, which may cause the electropolish process described herein to takes up to 30-60 min to planarize wide features. In one embodiment, the fluid dynamic boundary layer is formed using high substrate rotation speeds, such as about 100 to about 2000 rpm, which is believed to increase the plating/deplating current densities without any loss in the total leveling effect. At these rotational speeds it is believed that the electropolish process described herein can be shortened. Therefore, by

reducing the fluid dynamic boundary layer during the deposition and/or deplating process will greatly improve the throughput of the process. It should be noted that the fluid dynamic boundary layer thickness is related to the diffusion boundary layer thickness, which may affect the plating rate, dissolution rate, and final uniformity. In one embodiment, the fluid dynamic boundary layer is improved by increasing the rotation speed of the substrate during at least one part of the deposition and/or deplating process. In another embodiment, ultrasonic and/or megasonic actuators are positioned in the plating and/or deplating bath to reduce the fluid dynamic boundary layer during the processing. In this case it may be desirable to orient the megasonic or ultrasonic transducer such that the wave fronts of the so called "acoustic streaming" waves created in the fluid bath, propagate at a generally tangential orientation to the processing surface of the substrate. In another embodiment, it may be desirable to vibrate the surface of the substrate a frequency below a frequency that will avoid cavitation. In one aspect, it may be desirable to control the temperature of the electrolyte bath to change the fluid dynamic and/or kinetic diffusion properties.

[0048] In another embodiment, the fluid dynamic boundary layer is improved by increasing the fluid flow rate across the surface of the substrate. In one aspect, a planarization process is performed when the distance between the substrate and flow diffuser (e.g., a "porous material" membrane) is decreased until the distance is less than about 1 mm and a high flow of the electrolyte is delivered through the gap formed between the diffuser and the substrate. The flow diffuser may be a particle membrane, ionic membrane, regular ceramic diffuser or a counter electrode. An example of possible membranes that may be used are further described in the US Patent Application Publication Nos. 2004-0134775 A1, 2004-0035695 A1, and 2004-0016636 A1, which are all incorporated by reference in their entireties.

General Electropolishing Process Attributes

[0049] Generally, the electropolishing process of metalized substrates (e.g., copper containing metal layer) proceeds by means of cyclical repetition of electropolishing and electrochemical plating cycles. In one embodiment, the electropolishing process proceeds by means of alternating positive and negative potential/current pulses using in aqueous electrolyte that contains copper ions and a leveling agent.

[0050] During the electrochemical deposition step, the substrate is immersed in a copper plating electrolyte (e.g., ViaForm™ superfill electrolyte) that contains high effective leveling agents/additives, like dyes (Janus Green, UBAC, Alcyan blue etc), EBrite additives, thiourea and SPS derivatives, or any combinations of accelerator, suppressor and leveler (X, Y, Z additives), which may be used in copper superfill baths. Plating composition and concentration of additives are adjusted to use high cathodic current densities (up to 40-100 mA/cm²) and still have good surface leveling, or planarization, effect.

[0051] In one embodiment, the plating electrolyte contains a concentration of copper ions that is greater than about 0.2 mol/liter. In one embodiment, copper sulfate or copper pyrophosphate salts are used as the copper ion source. In another embodiment, to increase the planarization power, the electrolyte can optionally contain an inorganic acid,

(e.g., sulfuric acid, phosphoric acid or pyrophosphoric acid), various inorganic supporting salts, and other additives that may be used to improve the quality of plated and electropolished surfaces (e.g., oxidizers, surfactants, brighteners, etc.). The electrolyte composition can also be based on the alkaline copper plating baths (e.g., cyanide, pyrophosphoric, glycerin, ammonia, etc) as well.

[0052] In one embodiment, the bias is applied to the substrate has a square-waveform of alternating magnitude and/or alternating current direction (anodic and cathodic) (see FIGS. 2A-D). In one aspect, as shown in FIGS. 2A-D, the waveforms are alternating cathodic-anodic potential pulses. In other embodiments, the square-wave shaped pulses can be replaced by waveforms having other pulse profiles that include positive and negative current components (see FIGS. 2E-G).

[0053] In FIG. 3, the features of a single pulse cycle encompassing time periods t_c , t_p , and t_a is illustrated. In one aspect, the quantity of charge passed through the copper layer during the cathodic pulse period (Q_c) is equal to or only slightly lower than the quantity of charge passed during the anodic pulse period (Q_a). In one aspect, the magnitude of the amount of charge passed during the anodic pulse is defined as $1.3 Q_c > Q_a \geq Q_c$.

[0054] In one aspect, the duration of cathodic pulse (element t_c) varies from about 1 second to about 1000 seconds. It should be noted that the pulse frequency (e.g., 0.001 Hz to 1 Hz) is generally orders of magnitude different than conventional electrochemical pulse plating deposition, or electropolishing, processes.

[0055] In one aspect, using potentiostatic pulse electrolysis, the potential range for cathodic pulses is between about -0.1 v and about -0.4 v and the anodic pulses are between about +0.3 v and about +1.3 v. (vs. Cu/CuSO₄ (saturated) reference electrode).

[0056] In one aspect, using galvanostatic pulse electrolysis, the current range for cathodic pulses is between about 5 mA/cm² and about 60 mA/cm² and for the anodic pulses it is between about 20 mA/cm² and about 200 mA/cm². In one aspect, it may be desirable to add a pause between positive and negative pulses of a duration (t_p), which may be between about 0 and about 5 seconds.

[0057] In one aspect, the wafer's rotation speed can vary between about 10 and about 2000 rpm, however, to provide relatively fast and effective surface leveling, preferably one may use a rotation speed greater than about 100 rpm. In one aspect, the rotation speed can be different under cathodic and anodic periods.

[0058] In one aspect, to provide faster removal of very wide features (e.g., >200 um wide and >1 um high irregularities), the wafer-to-flow diffuser ("porous material") distance can be less than 1 mm and a high flow of the electrolyte through this gap has to be provided. As a flow diffuser ("porous material") may be a regular ceramic diffuser or a counter electrode.

Two Bath Electropolishing Process

[0059] In one embodiment of the electropolishing process sequence, a two bath electropolishing process is performed on a substrate that has substantially completed the gap fill process, but the features generally need not be completely

filled. In one aspect, the electropolishing process includes a periodic reverse planarization process that utilizes a two bath electropolishing process. The use of three separate electrolytes (i.e., gap fill electrolyte, electropolishing electrolyte and the planarizing electroplating electrolyte) allows each electrolyte bath to be optimized to perform either the gap fill process, the electropolishing process, or the electrochemical deposition step. In one aspect, the electrolyte used in the electrochemical deposition step contains a number of powerful levelers (discussed below) that help to planarize the surface of the substrate during the plating phase of the electropolishing process, and thus will generally not be useful to perform the gap fill process.

[0060] FIG. 4 illustrates one embodiment of an electrochemical cell that may be used to perform the electropolishing process. One will note that the common components that are well known in the art, such as electrical contact rings that electrically connects the metal layer on the substrate with the power supply, the substrate rinsing system, and additional fluid delivery valves required to replace one electrolyte with another electrolyte in electrode chambers are not shown in the FIG. 4. During processing both substrates 108, 110 can be rotated, or other means may be applied, to control the fluid dynamic boundary layer across the surface of the substrates 108, 110 inside the electrode chambers. In one embodiment, ultrasonic and/or megasonic actuators are positioned in the electrode chambers to reduce the fluid dynamic boundary layer on each substrate during processing. In this case it may be desirable to orient the megasonic or ultrasonic transducer such that the wave fronts of the so called "acoustic streaming" waves created in the fluid bath, propagate at a generally tangential orientation to the processing surface of the substrate. In one embodiment of the electropolishing process, the process steps are completed in cluster tool that has separate chambers that are adapted to perform the electropolishing step or the electrochemical deposition step. In one embodiment, a cluster tool may be adapted to perform gap filling with electrolyte in an ECP chamber mounted on the system, then perform electrochemical deposition in an electroplating chamber mounted on the system, and then perform electropolishing on an electropolishing chamber mounted on the system. A cluster tool that may be adapted to perform these steps is the SLIMCELL® ECP system, available from Applied Material, Inc., Santa Clara, Calif. Another example of an exemplary cluster tool that may be adapted to perform various aspect of the invention described herein is further described in the commonly assigned U.S. Pat. Nos. 6,635,157, 6,350,366, 6,699,380, and 7,025,862, which are all incorporated by reference in their entireties.

[0061] In one embodiment, the periodic reverse planarization (PRP) process, which is a subset of the electropolishing process described above, proceeds as follows. To help describe the periodic reverse planarization (PRP) process it is assumed that the substrate 108, 110 has an overburden layer is a 1 μm copper layer. It is also assumed that the amount of overburden left over after the planarization process is performed will be 0.1 μm and all irregularities (up to 100 μm in width and up to 0.5 μm in height) have been removed. It should be noted that this example and these assumptions are not intended to be limiting as to the scope of the invention described herein.

[0062] In one embodiment, the reverse planarization (PRP) process is used to planarize the substrates during both plating and deplating periods, due to the use of electrolytes that have each have a "leveling/polishing power." When electrolysis starts, one substrate is operating as a cathode (hereafter cathodic substrate), the other as an anode (hereafter anodic substrate). During processing the thickness of the metal layer on the surface of the cathodic substrate increases, but the height of undulation or surface features decreases due to the leveling components in the electrolyte. During processing the thickness of the metal layer on the surface of the anodic substrate decrease, and the height of undulation or surface features decreases due to the effect of the electropolishing process. In one aspect, it may not be desirable to remove enough material from the anodic substrate to cause a "terminal effect" problem in the subsequent deposition process step. The terminal effect, which is commonly found in plating processes, will affect the surface undulations and thus ability to planarize the substrate surface. In one aspect, it may be desirable to retain at least 500 $\text{\AA}$ of material on the field region after performing the electropolishing step to prevent the terminal effect in the subsequent electrochemical deposition step.

[0063] In one aspect, after performing each subsequent step the substrates are removed from their respective electrode chamber and their location are swapped so that the plated substrate can become an anode in polishing electrolyte, and the polished substrate can be plated on in the plating electrolyte. In one embodiment, instead of changing the location of the substrates by use of a robotic device, it may be desirable to exchange the various electrolytes that are delivered into electrode chamber and also change the polarity of the power supplies so that the opposite process can be performed on the substrate in the same electrode chamber. During the process of swapping the electrolytes, or the substrates, it may be desirable to rinse each electrode chamber and substrate with DI water and dry them using an air or nitrogen purge.

[0064] In the next step the electrochemical deposition step is performed on the previously electropolished substrate, and the electropolishing step is performed on the previously electrochemical deposited substrate. In one aspect, it may be desirable to cause the thickness on both substrates to be the same as it was initially (e.g., 1 μm) after the second step is performed. In this case the material thickness has not changed, but the height of surface features has decreased even more due to the leveling power achieved by the completion of both processes. Therefore, one can repeat these steps over and over again until a desired planarized height is achieved. When the surface becomes planarized enough, the last step then begins. In one embodiment, the last step may require that both substrates be electropolished to reduce the final copper thickness to a desired level and improve the final planarity. In one aspect, it may be desirable to reduce the overburden thickness to between about 0.05 μm and about 0.1 μm after completing the final step to reduce or remove the need for the "platen 1" polishing step commonly found in the subsequent CMP and ECMP processes.

[0065] Utilization of two separate electrolytes, instead of one in electrolyte that does both functions, will dramatically increase in the planarization efficiency both under plating and deplating, because the composition of the electrolytes

can be optimized for the desired process (i.e., electropolishing or electrochemical plating) to get the highest planarization efficiency at each step. Additionally, the usage of two substrates together in one planarization process increases the planarization throughput.

General Electropolishing Process Attributes

[0066] Generally, the electropolishing process of metalized substrates (e.g., copper containing metal layer) proceeds by means of cyclically repeating electropolishing and electrochemical plating cycles on each of the substrates.

[0067] During the electrochemical deposition step, the substrate is immersed in a copper plating electrolyte (e.g., ViaForm™ superfill electrolyte) that contains high effective leveling agents/additives (e.g., EBrite additives, UBAC additives, Janus Green). Plating composition and concentration of additives are adjusted to use high cathodic current densities (up to 40-100 mA/cm²) and still have good surface leveling effect.

[0068] During the electropolishing step, the substrate is immersed in any electropolishing electrolyte with good polishing/leveling power, for example, in phosphoric acid, phosphoric acid/sulfuric acid/water, phosphoric acid/alcohol blend, pyrophosphoric acid/water blend, etc. In one aspect, the components in the electrolyte (e.g., additives) are adjusted to use anodic current densities in the same current interval as in plating composition (up to 40-100 mA/cm²).

[0069] The electropolishing process, proceeds in an electrochemical cell 100 that has electrode chambers that may be adapted to perform both the electrochemical deposition step and the electropolishing step. In one embodiment, several electrochemical cells 100 (e.g., 2, 5, 25) can be combined in the one stack to perform the process in a batch type mode. In one aspect, the anodic electrode chambers are filled with the polishing electrolyte and the cathodic electrode chambers are filled with the copper plating electrolyte. In general, both electrolytes are circulating through their respective electrode chambers by means of one or more conventional fluid pumps. In one embodiment, the electrode chambers are separated from each other by a central compartment that has membranes 104 (e.g., microporous or ion-exchange membranes) separating it from the electrode chambers. In this configuration a mesh electrode 106 may also be positioned between membranes 104. In one embodiment, a flow the electropolishing electrolyte is delivered to the central compartment during processing. The mesh electrode 106 in the central compartment can be made of copper, graphite fiber, platinum wire, etc.

[0070] The electropolishing process proceeds so that one of the two substrates are initially deposited on using the electrochemical deposition step using the plating electrolyte, and the other substrate is electropolished using the electropolishing step and the polishing electrolyte. In one aspect, after a desired time the substrates swap locations so that the plated substrate can be becomes an anode in polishing electrolyte, and the polished substrate can be the cathode in the plating electrolyte. In one embodiment, instead of changing the location of the substrates by use of a robotic device, it may be desirable to change which electrode chamber the various electrolytes are delivered into during processing and polarity of the power supplies need to be switched so that the opposite process can be performed on the substrate. During

the process of swapping the electrolytes or the substrates it may be desirable to rinse each electrode chamber and substrate with DI water and dry all of them using an air or nitrogen purge.

[0071] Since it is often desirable for the final copper thickness on the substrate to a small as possible it may be desirable to use the polishing step as the final step of the electropolishing process. In this final step, all chambers will be filled with the polishing electrolyte and the mesh electrode 106 disposed near the membranes is biased cathodically, while the substrates are biased anodically.

Periodic Reverse Copper Planarization

[0072] In one embodiment of the invention, electropolishing a substrate may be performed using a deplating-plating cycle. During the plating cycle, the substrate is exposed to an electrolyte plating solution that contains highly effective leveling agents and additives (e.g., VIAFORM™ superfill electrolyte, EBrite additives, UBAC™ additives, Janus Green, etc.). The electrolyte plating solution and the concentration of the additives and leveling agents are adjusted for use with high cathodic current densities to produce good surface leveling effects. In one embodiment, the current density is about 30 to about 100 mA/cm². In another embodiment, the current density is about 40 to about 60 mA/cm².

[0073] During the deplating cycle, the substrate is exposed to an electrolyte polishing solution with good polishing/leveling power. Suitable electrolyte polishing solutions may include a phosphoric acid, phosphoric acid/sulfuric acid/water, phosphoric acid/alcohol blend, pyrophosphoric acid/water blend, etidronic acid, and blends of the acids with one another, with water, or with organic solvents such as alcohols, glycols, ethanolamines or some inorganic acids such as sulfuric acid and nitric acid, 85% H₂PO₄, H₃PO₄—H₂SO₄—H₂O blends, H₃PO₄ blends with alcohols and glycols. To increase the planarization effect, some oxidizers such as Fe(III) and hydrogen peroxide may be added to the electrolyte polishing solution. The electrolyte polishing solution and concentration of the electrolyte polishing solution is adjusted to use current densities in the same range as in the plating cycle.

[0074] The electropolishing process may be performed in an electrochemical cell with alternating anodic and cathodic compartments. One embodiment of an electrochemical cell 100 in which a method of electropolishing may be practiced is shown in FIG. 4. The cell 100 has a body 130 that includes plating and electropolishing compartments 120, 118 separated by a common cathode 106. Membranes 104 isolate the cathode 106 from substrates 108, 110 disposed in the compartments 120, 118. In the embodiment depicted in FIG. 4, the substrates 108, 110 have a vertical orientation in the compartments 120, 118. The membranes 104 can be microporous membranes or ion-exchange membranes. The electrode 106 may be a mesh of perforated plate, and may be made of copper, graphite fiber, platinum, or other suitable material.

[0075] The cell 100 is powered by a power supply 102 suitable for producing current densities in the cell as described above. The power supply 102 is coupled between the electrodes 108, 110 and the cathode 106, and can provide a direct current or an alternating current. Several cells 100

can be combined into one stack. Up to five electropolishing cells **100** can be used in one stack. Both the electrolyte polishing solution and the electrolyte plating solution may be recirculated and reused in the cell **100**. Alternatively, the electrolyte polishing solution and the electrolyte plating solution may be used only one time and then may be disposed of.

[0076] The polishing electrolyte tank **114** is filled with the electrolyte polishing solution and the plating electrolyte tank **112** is filled with the electrolyte plating solution. The pumps **116** circulate the electrolytes through the compartments **118**, **120** from the tanks **112**, **114**.

[0077] Electropolishing using the electropolishing cell of the present invention involves operating one substrate as the cathode and one as the anode. The anode will be polished, and the cathode will be plated. After a particular period of processing, the substrates will need to change processing conditions. The particular period of processing will depend upon the initial layer thickness on the substrate, the features heights, and the features widths.

[0078] The processing conditions can change by physically changing the location of the substrates so that the substrate that was processed in the electrolyte plating solution is placed in the electrolyte polishing solution and the substrate that was in the electrolyte polishing solution is placed in the electrolyte plating solution.

[0079] In an alternate embodiment, the substrate can remain in place and the type of electrolyte will change. For example, the substrate—anode **110** can remain in the polishing compartment **118**. The electrolyte can be drained from the polishing compartment **118**. The substrate—anode **110** and compartment **118** are quickly rinsed with deionized water. Then, new electrolyte is provided to the compartment **118** so that the compartment **118** now becomes a plating compartment. Likewise, the electrolyte is drained from the plating compartment **120**, the substrate—cathode **108** and compartment **120** are rinsed in deionized water, and the electrolyte is replaced so that the plating compartment **120** becomes a polishing compartment. The electrolyte can be drained from the tank in a few seconds.

[0080] The process of swapping substrate locations or changing the type of electrolyte between the compartments can be repeated multiple times until a desired level of planarization is achieved. FIG. 5 shows a chart that follows the progress of two substrates A, B through the electroplanarization process. Before any planarization, the two substrates A, B each have a layer deposited thereon that have roughly the same thickness, feature height, and feature width. After the first step, the first substrate A has been plated and the second substrate B has been deplated or polished. In the second step, the first substrate A will be polished and the second substrate B will be plated to complete a first cycle. After the second step, the substrates A, B are quite similar in terms of the planarization. During the third step, the first substrate A is again plated and the second substrate B is deplated or polished as a second cycle begins. During the fourth step, the first substrate A is polished or deplated and the second substrate B is plated. Again, after the fourth step, both substrates A, B are quite similar in terms of the planarization. The plating/polishing cycle will continue until a satisfactory level of planarization has been achieved. In one embodiment, the substrates A, B

will pass through the planarization cycle about 6 to about 10 times. An average cycle time may be about 5 minutes to about 14 minutes. It should be noted that the polishing and plating steps may be cycled more or less times, and/or for different time periods, than described above.

[0081] By using two electrolytes rather than a single electrolyte that operates as both the anolyte and the catholyte, the planarization efficiency is dramatically increased during both the plating and polishing because both electrolytes may be optimized to achieve the highest planarization performance and efficiency. By processing two substrates simultaneously in one plating cell, substrate throughput may be increased as well.

[0082] While not shown in FIG. 4, electrical contact rings will provide the electrical connection between the substrates **108**, **110** and the power supply **102**. Additionally, the substrates **108**, **110** may be rotated and the electrolytes may be stirred by mechanical means.

EXAMPLE

[0083] An example will be described below in which two substrates are processed within the electroplanarization cell of the present invention. The substrates have a 1 μm thick copper layer thereon that has a feature that is to be filled and planarized. The thickness is exemplary, as other thicknesses may be used. When the process starts, one substrate will operate as the cathode and the other substrate as the anode. On the substrate-cathode side, the thickness of the copper layer will increase, but the height of the feature will decrease because material will be deposited with the feature. On the substrate-anode side, the thickness of the copper layer will decrease, and the height of the feature will decrease as well because material is being removed. The process begins by removing a portion of the copper layer, for example, up to about 0.9 μm , from the first substrate. The copper layer is not entirely removed to minimize the terminal effect in copper plating-deplating uniformity. After a portion of the copper layer has been removed from the first substrate, the process is stopped. As the material is removed from the first substrate, material is added to the second substrate. In one embodiment, the thickness on the substrate-anode side will be 0.1 μm and the thickness on the substrate-cathode side will be 1.9 μm after the first cycle. At this point, the substrate will either swap locations or the electrolyte will be switched. Now the process continues by performing a second cycle in which the second substrate is plated and the first substrate is polished. Again, the thickness of the layers will change by about 0.9 μm . Following the second step, the thickness on the substrate will be about the same as it was initially (i.e., about 1 μm), but the height of the features is decreased. The process steps then continue until all of the surface irregularities are completely removed. Once the substrates are sufficiently planarized, both substrates are biased as a cathode and electropolished with an electrolyte polishing solution to remove the excessive copper layer thickness. During the last step, about 0.9 μm is removed from each substrate to complete the electroplanarization.

Cooling

[0084] To further promote efficient electropolishing, the surface of the layer being polished can be cooled down to a temperature that is close to or below the freezing point of the polishing electrolyte while the temperature of the electrolyte

is provided at close to room temperature or greater. FIG. 6 is a sectional view of one embodiment of an electroprocessing cell 300 suitable for cooling a substrate 316 during processing. The cell 300 includes a cathode chamber 306, electrolyte 304, cathode 306, membrane 308, susceptor 310, cooling fluid inlet 312, and cooling fluid outlet 314. The susceptor 310 is rotatable and maintains the substrate 316 about 0.5 to about 5 mm from the membrane 308. In one embodiment, the substrate 316 is arranged face up to provide a high temperature gradient in the electrolyte present between the substrate 316 and the membrane 308.

[0085] To control the substrate's temperature, a chilled liquid is circulated through the susceptor 310 between a cooling fluid inlet 312 and outlet 314. The liquid may have a freezing point below that of the electrolyte. In one embodiment, the substrate 316 is precooled before it comes into contact with the electrolyte. The precooling may be performed by exposing the substrate 316 to liquid nitrogen, liquid air, or other similar coolant. The exposing may occur within or remotely from the cell 300 before processing. The liquid coolant may flow across the surface of the substrate to precool the substrate. Alternatively, the susceptor 310 may include a thermoelectric cooler.

[0086] In order to maintain a constant electropolishing electrolyte temperature and the temperature gradient between the substrate's surface and the electrolyte, the electropolishing electrolyte can circulate along the sides of the susceptor 310 (See FIG. 3).

[0087] Regular copper electropolishing electrolytes include 85 percent H_2PO_4 , H_3PO_4 — H_2SO_4 — H_2O blends, H_3PO_4 blends with alcohols and glycols. The electrolytes have relatively high freezing points that are above 0 degrees Celsius. For example, concentrated phosphoric acid freezes at about 42 degrees Celsius, pyrophosphoric acid freezes at about 61 degrees Celsius, and blends with high (95 percent) glycerin content at 10 degrees Celsius. Hence, it is relatively easy to cool the substrate's surface to below the electrolyte freezing temperature. The convectional flow near the surface will become zero because of crystallization and viscosity increases that occur as the electrolyte nears its freezing point.

[0088] Although the substrate may be cooled to low temperatures (i.e., to about -20 degrees Celsius), the temperature in the electrolyte may be in the range of about 25 degrees Celsius to about 50 degrees Celsius. The temperature gradient in the electrolyte at the substrate-electrolyte boundary will still be relatively small, about $0.1\text{--}1^\circ\text{C}/\mu\text{m}$. When the temperature of the electrolyte near the substrate surface is close to the freezing point, the thermal gradient evokes other gradients that increase the peaks-to-valleys current contrast. With crystallization and viscosity higher in the recesses (i.e., when the temperature is lower), the final polishing effect is increased. The viscosity near the freezing point increases dramatically for polishing electrolytes, up to ten times per 10 degrees Celsius. The increase in viscosity gradient causes the top-to-valley dissolution contact to become much more expressed than at regular electropolishing.

[0089] FIG. 6 shows the electropolishing cell in which a high thermal gradient may be achieved. In this case, the substrate 316 is laying face up on the cooling susceptor 310. The perforated cathode 306 removes hydrogen bubbles that

form and is separated from the substrate 316 by a flat, porous membrane 308. Both the orientation of the substrate 316 and the position of the membrane 308 are selected to minimize the natural convection and hence, to increase the temperature gradient. Additionally, the membrane 308 to substrate 316 distance is minimal (i.e., about 0.5 to about 2 mm). The rotation of the substrate 316, the rotation of the cathode 306, the recirculation of the electrolyte through the membrane 308, and the movement of the electrolyte thorough the membrane-substrate gap can help improved planarization.

Auxiliary Cell

[0090] The auxiliary cell is a small cell (relative to the diameter of the substrate) that can move along the substrate surface without touching by means of a robotic arm. The auxiliary cell 500 may be located above the electroplating cell 400 as shown in FIG. 7. The electroplating cell 500 comprises a diffuser 402, a membrane 404, pumps 406 for providing electrolyte, an anolyte tank 408, a catholyte tank 410, and a substrate 414 held by a contact ring 416. A backing plate 502 is disposed behind the substrate 414, and the substrate 414 is spaced from the contact ring 416 by contact pins 504. Electrolyte is provided from an electrolyte tank 412 to the auxiliary cell 500. The auxiliary cell 500 is best shown in FIG. 8 and comprises a diffuser 506, an inner vessel 508, an electrode 510, an inlet manifold 512, an outlet manifold 514, an outer vessel 516, and robotic arm 518. In one embodiment, a dosing pump can be provided. The auxiliary cell 500 can be shaped to improve the current uniformity on the substrate 414. The outer vessel 516 of the cell 500 is convex; the curvature is close to the substrate's diameter to provide good electrolyte contact with the contact pins 504 at the beginning of the treatment.

[0091] Initially, before the treatment starts, the substrate 414 is placed in the contact ring 416 and sealed by the backing plate 502 while the cell 500 is below. The substrate 414 starts to rotate and moves down to the auxiliary position. In the auxiliary position, the distance between the upper flat surface of the inner vessel 508 and the substrate 414 is about 0.2 to about 3 mm.

[0092] The electrolyte 520 from the electrolyte tank 414 moves up into the inner vessel 508 by means of a pump 406 and flows out through the cell rim into the outer vessel 516 and returns to the electrolyte tank 414 again. Because the substrate to cell gap is small, the electrolyte wetting power is enough to keep the electrolyte within the gap and to provide a robust electrical and chemical contact between the electrolyte and the substrate.

[0093] In operation, the cell 500 moves along the substrate's surface from the substrate edge to the center while the substrate continues to rotate. The rate of the cell movement to the substrate's center slowly increases so that each substrate spot is treated for approximately the same amount of time.

[0094] After the treatment, the cell 500 is moved aside while the substrate 414 is moved to the electroplating position. The auxiliary cell 500 can be used anytime when the formation of a layer on the substrate 414 needs any additional chemical or electrochemical treatment to improve the ECP process. For example, formation of ultra-thin electrochemical copper seed layers (about 10 to about 50 Å thick) on noble barriers (Ru, Ir, Os, etc.). Other possible uses

include: initial gap fill of the most aggressive and small features on the resistive pattern substrates, the first gap fill step in a two step plating process to get copper deposits with maximum planarity, grafting, electroless formation of other metal layers on barrier metals or copper, chemical/electrochemical pretreatment and post-treatment of substrates like surface activation, cleaning, and copper protection, and electropolishing the contact ring to remove and clean material from the contact ring that have been deposited in previous processes. Depending upon the process specialties, the chemistry used in the cell **500**, the flow rates, and the current densities, the treatment time will vary. The cell **500** can provide more than one chemical/electrochemical operation. In such a situation, the cell **500** can be fed by different solutions from several small vessels successively.

[0095] The small size of the cell (i.e., smaller than the substrate) eliminates or dramatically minimizes the terminal effect. The terminal effect causes copper not to be efficiently plated in the center of the substrate without sophisticated hardware and technology. The small size of the cell (together with the resistive diffuser inside the cell) make the plating relatively uniform. Additionally, the cell may be designed so that the outer vessel sidewall is convex and copies the substrate's diameter curvature to completely wet the contact ring before the plating starts. Without completely wetting the contact ring, the heat evolving near the electrical contact can be high enough to peel off the resistive barrier layer and damage the substrate. The oblong shape of the cell helps to minimize the steps of cell movements and the total time of plating.

[0096] FIG. 9A shows how a seed layer can be formed by three consecutive movements of the cell **500** from the edge to the center while substrate **600** is rotating. The cell may be in the first position **602** to plate the first zone **608**. The cell **500** may be in the second position **604** to place the second zone **610**. The cell **500** may be in the third position **606** to plate the third zone **612**.

[0097] FIG. 9B shows how a seed layer may be formed by following a spiral path **618**. The auxiliary cell **500** may follow the spiral path **618** to plate the substrate. To form a copper seed layer of about 20 Å thick, the cell will need only 5 to 8 seconds depending upon the current density used (i.e., about 10 to about 40 mA/cm²).

[0098] The small amounts of copper plated by the cell require a minimal volume of electrolyte to plate about 200 to about 300 substrates. In one embodiment, the electrolyte tank **412** holds only about 1 to about 2 liters. The chemical composition of the electrolyte used in the cell **500** may be different from that used in the main electroplating cell **400**. For example, the electrolyte used in the cell **500** may be more acidic or contain different concentrations of additives.

[0099] After the seed layer is formed, the robotic arm **518** moves the cell **500** aside while the substrate **414** is moved to the main electroplating cell **400** for the next step of plating. The presence of the seed layer on the substrate **414** simplifies the copper plating. The chemistry in the auxiliary cell is optimized for the effective gap fill while the chemistry in the main cell is optimized to get the maximum surface planarity of the copper being deposited. The copper plating may be performed without any anode segmentation, additional power supplies, low conductivity anolyte, small wafer to collimator distances, or complicated current recipes. A

very high acidic catholyte is not required in the main cell. The auxiliary cell has already nucleated the substrate with the seed layer.

[0100] 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.

We claim:

1. A method for electropolishing, comprising:

a) cyclically processing a substrate to planarize an exposed conductive layer:

i) exposing the conductive layer to a catholyte solution of a first chemistry; and

ii) exposing the conductive layer to an anolyte solution of a second chemistry; and

b) detecting an endpoint of the planarization process.

2. The method of claim 1, wherein the cyclical process further comprises:

exposing the conductive layer in a vertical orientation to the first and second chemistries.

3. The method of claim 1, wherein the cyclical process further comprises:

transferring the substrate between separate compartments of an electropolishing cell, wherein each compartment is configured to supply either the first or the second chemistry.

4. The method of claim 1, wherein the cyclical process further comprises:

filling a compartment of an electropolishing cell with the catholyte solution of the first chemistry; and

draining the catholyte solution of the first chemistry from the first compartment; and

filling the compartment of the electropolishing cell with the anolyte solution of the second chemistry.

5. The method of claim 1, wherein the catholyte solution of the first chemistry and the anolyte solution of the second chemistry are recirculated.

6. The method of claim 1, wherein exposing the conductive layer to the catholyte solution further comprises:

cooling the substrate to a temperature below or about the freezing point of the catholyte of the first chemistry.

7. The method of claim 1, wherein exposing the conductive layer to the anolyte solution further comprises:

cooling the substrate to a temperature below or about the freezing point of the anolyte solution of the first chemistry.

8. A method for electropolishing, comprising:

providing a first and a second substrate, wherein each substrate has a layer deposited thereon;

performing a first sequence of:

exposing the layer of the first substrate to a catholyte solution of a first chemistry;

exposing the layer of the second substrate to an anolyte solution of a second chemistry;

providing a current density to both the first catholyte solution and the first anolyte solution;

performing a second sequence of:

exposing the layer of the first substrate to an anolyte solution of the second chemistry;

exposing the layer of the second substrate to a catholyte solution of the first chemistry;

providing a second current density to both the second catholyte solution and the second anolyte solution;

repeating at least one of the first and second sequences.

9. The method of claim 8, wherein the providing the first and second substrates further comprises:

placing the first and second substrates vertically in separate compartments of an electropolishing cell.

10. The method of claim 9, further comprising:

providing the catholyte solution of the first chemistry to the first compartment and providing the anolyte solution of the second chemistry to the second compartment during the first sequence;

draining the catholyte solution of the first chemistry from the first compartment and draining the anolyte solution of the second chemistry from the second compartment; and

providing the catholyte solution of the first chemistry to the second compartment and providing the anolyte solution of the second chemistry to the first compartment during the second sequence.

11. The method of claim 10, further comprising:

providing the catholyte solution of the first chemistry to the first compartment and providing the anolyte solution of the second chemistry to the second compartment during the first sequence;

removing the first substrate from the first compartment and placing it in the second compartment; and

removing the second substrate from the second compartment and placing it in the first compartment.

12. The method of claim 9, wherein the catholyte solution of the first chemistry and the anolyte solution of the second chemistry are recirculated.

13. The method of claim 9, further comprising:

cooling the first substrate to a temperature below or about the freezing point of the catholyte of the first chemistry during the first sequence; and

cooling the second substrate to a temperature below or about the freezing point of the catholyte of the first chemistry during the second sequence.

14. The method of claim 13, further comprising:

cooling the second substrate to a temperature below or about the freezing point of the anolyte of the second chemistry during the first sequence; and

cooling the first substrate to a temperature below or about the freezing point of the anolyte of the second chemistry during the second sequence.

15. A method for electropolishing, comprising:

providing a substrate on a substrate chuck within an electropolishing cell, wherein the substrate has a layer deposited thereon;

contacting an electrolyte to the layer on the substrate within the electropolishing cell;

cooling the substrate to a temperature below or about the freezing point of the electrolyte; and

electropolishing the layer on the substrate.

16. The method of claim 15, wherein cooling further comprises:

establishing a temperature gradient of about $0.1^{\circ}\text{C}/\mu\text{m}$ to about $1^{\circ}\text{C}/\mu\text{m}$ at the interface of the substrate and the electrolyte.

17. A method of depositing a seed layer, comprising:

positioning a surface of a rotating substrate proximate to but not touching an auxiliary cell;

moving the auxiliary cell across the surface of the substrate;

flowing an electrolyte between an inner vessel and an outer vessel of the auxiliary cell and into contact with the surface of the substrate, wherein the outer vessel surrounds the inner vessel; and

applying power to an electrode in fluid contact with the electrolyte.

18. An apparatus, comprising:

a contact ring configured to retain a substrate against a substrate support;

an electroplating cell;

a robotic arm; and

an auxiliary cell coupled to the robotic arm, wherein the auxiliary cell is located between the contact ring and electroplating cell and wherein the auxiliary cell comprises:

a chamber connected to the arm, wherein the chamber has an outer vessel surrounding an inner vessel and wherein electrolyte within the inner vessel can overflow into the outer vessel, a diameter of the outer vessel is small relative to the diameter of the substrate;

an electrode within the inner vessel;

a diffuser within the inner vessel;

an inlet manifold coupled to the inner vessel; and

an outlet manifold coupled to the outer vessel.

19. The apparatus of claim 18, wherein the inlet is coupled to an electrolyte source.

20. The apparatus of claim 18, wherein the outlet is coupled to the electrolyte source.

21. The apparatus of claim 18, wherein the contact ring and substrate support are moveable between a raised position and a lowered position.