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(71) Applicant (*for all designated States except US*): APPLIED MATERIALS, INC. [US/US]; 3050 Bowers Avenue, Santa Clara, CA 95054 (US).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): LIU, Feng, Q. [CN/US]; 4729 Lago Vista Circle, San Jose, CA 95129 (US). CHEN, Liang-Yuh [—/US]; 1400 Melbourne Street, Foster City, CA 94404 (US). TSAI, Stan, D. [US/US]; 5444 Dekker Terrace, Fremont, CA 94555 (US). DUBOUST, Alain [US/US]; 668 Bryan Avenue, Sunnyvale, CA 94086 (US). NEO, Siew, S. [SG/US]; 1556 Halford Ave., Suite 292, San Jose, CA 95051 (US). HU, Yongqi [CN/US]; 1823 Parkview Green Circle, San Jose, CA 95131 (US). WANG, Yan [US/US]; 920 Rockefeller Drive, 11B, Sunnyvale, CA 94087 (US). BUTTERFIELD, Paul, D. [US/US]; 1684 Kevin Drive, San Jose, CA 95124 (US).

(74) Agents: PATTERSON, B., Todd et al.; Moser, Patterson & Sheridan, LLP, 3040 Post Oak Blvd., Suite 1500, Houston, TX 77056 (US).

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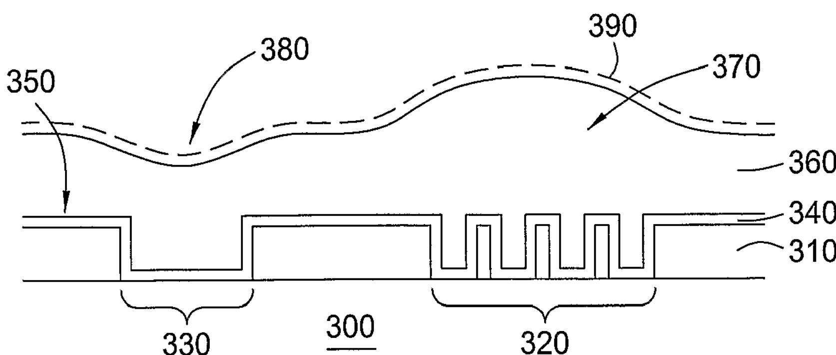

(57) Abstract: A method of processing a substrate having a conductive material layer disposed thereon is provided which includes positioning the substrate in a process apparatus and supplying a first polishing composition between to the substrate. The polishing composition comprises phosphoric acid, at least one chelating agent, a corrosion inhibitor, a salt, an oxidizer, abrasive particulates, at least one pH adjusting agent to provide a pH from about 4 to about 7 and a solvent. The method further includes forming a passivation layer on the conductive material layer, removing the passivation layer to expose a portion of the conductive material layer, applying a first bias to the substrate, and removing at least about 50% of the conductive material layer. The method further includes separating the substrate from the first polishing composition, exposing the substrate to a second polishing composition and a second bias, and continuing to remove the conductive material layer.

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POLISHING COMPOSITION AND METHOD FOR POLISHING A CONDUCTIVE MATERIAL.

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] Embodiments of the present invention relate to compositions and methods for removing a conductive material from a substrate.

Background of the Related Art

[0002] 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 processing capabilities. Reliable formation of interconnects is important to VLSI and ULSI success and to the continued effort to increase circuit density and quality of individual substrates and die.

[0003] Multilevel interconnects are formed using sequential material deposition and material removal techniques on a substrate surface to form features therein. As layers of materials are sequentially deposited and removed, the uppermost surface of the substrate may become non-planar across its surface and require planarization prior to further processing. Planarization or "polishing" is a process where material is removed from the surface of the substrate to form a generally even, planar surface. Planarization is useful in removing excess deposited material, removing undesired surface topography, and surface defects, such as surface roughness, agglomerated materials, crystal lattice damage, scratches and contaminated layers or materials to provide an even surface for subsequent photolithography and other semiconductor processes.

[0004] Chemical mechanical planarization or chemical mechanical polishing (CMP) is a common technique used to planarize substrates. In conventional CMP techniques, a substrate carrier or polishing head is mounted on a carrier assembly

and positioned in contact with a polishing article in a CMP apparatus. The carrier assembly provides a controllable pressure to the substrate urging the substrate against the polishing pad. The pad is moved relative to the substrate by an external driving force. Thus, the CMP apparatus effects polishing or rubbing movement between the surface of the substrate and the polishing article while dispersing a polishing composition to effect both chemical activity and mechanical activity.

[0005] However, materials deposited on the surface of a substrate to fill feature definitions formed therein often result in unevenly formed surfaces over feature definitions of variable density. Referring to Figure 1A, a metal layer 20 is deposited on a substrate 10 to fill wide feature definitions 30, also known as low density feature definitions, or narrow feature definitions 40, also known as and high density feature definitions. Excess material, called overburden, may be formed with a greater thickness 45 over the narrow feature definitions 40 and may have minimal deposition 35 over wide feature definitions 30. Polishing of surfaces with overburden may result in the retention of residues 50 from inadequate metal removal over narrow features. Overpolishing processes to remove such residues 50 may result in excess metal removal over wide feature definitions 30. Excess metal removal can form topographical defects, such as concavities or depressions known as dishing 55, over wide features, as shown in Figure 1B.

[0006] Dishing of features and retention of residues on the substrate surface are undesirable since dishing and residues may detrimentally affect subsequent processing of the substrate. For example, dishing results in a non-planar surface that impairs the ability to print high-resolution lines during subsequent photolithographic steps and detrimentally affects subsequent surface topography of the substrate, which affects device formation and yields. Dishing also detrimentally affects the performance of devices by lowering the conductance and increasing the resistance of the devices, causing device variability and device yield loss. Residues may lead to uneven polishing of subsequent materials, such as barrier layer materials (not shown) disposed between the conductive material and the substrate surface. Post CMP profiles generally show higher dishing on wide trenches than on narrow trenches or dense areas. Uneven polishing will also increase defect formation in devices and reduce substrate yields.

[0007] Also, substrate polishing processes must be very efficient to increase the throughput production. Often, defects are formed on substrates that are over polished due to an increase in process variables, such as chemical concentrations, electrical potentials and/or pressure of polishing articles. Some of these defects may be minimized by decreasing these variables, but with an increase of time and loss of throughput production.

[0008] Therefore, there is a need for compositions and methods for removing conductive material from a substrate that minimizes damage to the substrate during planarization, as well as minimizes time for production.

SUMMARY OF THE INVENTION

[0009] In one embodiment, a method of processing a substrate having a conductive material layer disposed thereon is provided which includes positioning the substrate in a process apparatus and supplying a first polishing composition to the substrate. The polishing composition comprises phosphoric acid, at least one chelating agent, a corrosion inhibitor, a salt, an oxidizer, abrasive particulates, at least one pH adjusting agent to provide a pH from about 4 to about 7, and a solvent. The method further includes forming a passivation layer on the conductive material layer, removing the passivation layer to expose a portion of the conductive material layer, applying a first bias to the substrate, and removing at least about 50% of the conductive material layer. The method may further include separating the substrate from the first polishing composition, exposing the substrate to a second polishing composition and a second bias, and continuing to remove the conductive material layer.

[0010] In another embodiment, a method of processing a substrate having a conductive material layer disposed thereon is provided which includes positioning the substrate on a process apparatus and exposing the substrate to a first polishing composition comprising phosphoric acid, at least one chelating agent, a corrosion inhibitor, a salt, an oxidizer and abrasive particulates. The method further includes applying a first bias to the substrate, removing at least 50% of the conductive material layer, exposing the substrate to a second polishing composition and a second bias and continuing to remove the conductive material layer.

[0011] In another embodiment, a method of removing a conductive material layer is provided which includes providing the substrate to a process apparatus and exposing the substrate to a first polishing composition. The first polishing composition comprises from about 1 wt% to about 10 wt% of phosphoric acid, from about 0.1 wt% to about 6 wt% of at least one chelating agent, from about 0.01 wt% to about 1 wt% of a corrosion inhibitor, from about 0.5 wt% to about 10 wt% of a salt, from about 0.2 wt% to about 5 wt% of an oxidizer, from about 0.05 wt% to about 1 wt% of an abrasive particulates, at least one pH adjusting agent to provide a pH from about 4 to about 7, and a solvent. The method further includes applying a first bias to the substrate, removing at least 50% of the conductive material layer, and exposing the substrate to a second polishing composition and a second bias to continue removing the conductive layer. The second polishing composition comprises about 0.1 wt% to about 5 wt% of phosphoric acid, from about 0.1 wt% to about 5 wt% of at least one chelating agent, and from about 0.01 wt% to about 1 wt% of the corrosion inhibitor.

[0012] In another embodiment, a method of processing a substrate having a conductive material layer disposed thereon is provided which includes positioning the substrate in a process apparatus, exposing the substrate to a first polishing composition with a first conductivity in a range from about 30 milliSiemens (mS) to about 60 mS, the first polishing composition comprising an oxidizer and abrasive particulates, and applying a first bias to the substrate. The method may further include exposing the substrate to a second polishing composition with a second conductivity in a range from about 15 mS to about 40 mS, and applying a second bias to the substrate to continue removing the conductive layer.

[0013] In another embodiment, a method of processing a substrate having a conductive material layer disposed thereon is provided which includes positioning the substrate in a process apparatus, exposing the substrate to a first polishing composition, and applying a first bias to the substrate. The first polishing composition includes phosphoric acid, at least one chelating agent, a corrosion inhibitor, a salt, an oxidizer, abrasive particulates, at least one pH adjusting agent to provide a pH from about 4 to about 7, and a solvent. The process further includes exposing the substrate to a second polishing composition, applying a second bias to

the substrate, and continues removing the conductive layer. The second polishing composition comprises phosphoric acid, at least one chelating agent, a corrosion inhibitor, abrasive particulates, at least one pH adjusting agent to provide a pH from about 4 to about 7, and a solvent.

[0014] Further embodiments of the invention provide compositions and methods for removing conductive materials by an electrochemical mechanical polishing technique. In one aspect, a method is provided for processing a substrate having a conductive material layer disposed thereon including providing the substrate to a process apparatus comprising a first electrode and a second electrode with the substrate in electrical contact with the second electrode, wherein the substrate surface comprises conductive material layer disposed over narrow feature definitions and wide feature definitions, supplying a polishing composition between the first electrode and the substrate, wherein the polishing composition comprises an acid based electrolyte system, one or more chelating agents, greater than about 0.2 wt.% of one or more corrosion inhibitors, one or more inorganic or organic acid salts, one or more pH adjusting agents to provide a pH between greater than about 4.5 and about 7, and a solvent, wherein the polishing composition forms a passivation layer on the conductive material, removing the passivation layer to expose a portion of the conductive material, applying a bias between the first electrode and the second electrode, and removing conductive material disposed over narrow feature definitions at a higher removal rate than conductive material disposed over wide feature definitions. Removing material over the narrow feature definitions at a higher removal rate may result in the formation of a protrusion over the wider feature definition using the composition described herein.

[0015] The protrusion formation may also be accomplished by applying power by a pulse modulation technique between the first electrode and the second electrode to remove conductive material disposed over narrow feature definitions at a higher removal rate than conductive material disposed over wide feature definitions.

[0016] The method also further includes polishing the substrate by at least a chemical mechanical polishing process. The chemical mechanical polishing process may be a chemical mechanical polishing process or a second

electrochemical mechanical polishing process. The electrochemical mechanical polishing process may be performed on a first platen as described herein, the chemical mechanical polishing process may be performed on a conventional chemical mechanical polishing platen, and the second electrochemical mechanical polishing process may be performed on the same or different platen adapted for electrochemical mechanical polishing, such as the second platen as described herein. The method may comprise polishing the substrate initially with an electrochemical mechanical process and then with a chemical mechanical polishing process or a second electrochemical mechanical process adapted to remove conductive material disposed over wide feature definitions at a removal rate greater than or equal to the removal rate of conductive material disposed over narrow feature definitions. The second electrochemical mechanical process may have a corrosion inhibitor concentration less than the first electrochemical mechanical process and/or have a pH less than the first electrochemical mechanical process.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] So that the manner in which the above recited aspects of the present invention are attained and can be understood in detail, a more particular description of embodiments of the invention, briefly summarized above, may be had by reference to the embodiments thereof which are illustrated in the appended drawings.

[0018] 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.

[0019] Figures 1A-1B are schematic cross-sectional views illustrating a polishing process performed on a substrate according to conventional processes;

[0020] Figure 2 is a plan view of one embodiment of a processing apparatus of the invention;

[0021] Figure 3 is a cross-sectional view of one embodiment of a polishing process station;

[0022] Figures 3A is a schematic cross-sectional view of one embodiment of a conductive article 203;

[0023] Figures 4A-4D are schematic cross-sectional views illustrating a polishing process performed on a substrate according to one embodiment for planarizing a substrate surface described herein; and

[0024] Figures 5A-5E are schematic cross-sectional views illustrating a polishing process performed on a substrate according to another embodiment for planarizing a substrate surface described herein.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0025] In general, aspects of the inventions provide compositions and methods for removing at least a conductive material from a substrate surface. The inventions are described below in reference to a planarizing process for the removal of conductive materials from a substrate surface by an electrochemical mechanical polishing (ECMP) technique.

[0026] The words and phrases used herein should be given their ordinary and customary meaning in the art by one skilled in the art unless otherwise further defined. Chemical mechanical polishing should be broadly construed and includes, but is not limited to, planarizing a substrate surface using chemical activity and mechanical activity, or a concurrent application of chemical activity and mechanical activity. Electropolishing should be broadly construed and includes, but is not limited to, removing material from a substrate by eroding the substrate surface under application of current. Electrochemical mechanical polishing (ECMP) should be broadly construed and includes, but is not limited to, planarizing a substrate by the application of electrochemical activity, mechanical activity, chemical activity, or a concurrent application of a combination of electrochemical, chemical, and/or mechanical activity to remove material from a substrate surface.

[0027] Anodic dissolution should be broadly construed and includes, but is not limited to, the application of an anodic bias to a substrate directly or indirectly which results in the removal of conductive material from a substrate surface and into a surrounding polishing composition. Polishing composition should be broadly

construed and includes, but is not limited to, a composition that provides ionic conductivity, and thus, electrical conductivity, in a liquid medium, which generally comprises materials known as electrolyte components. The amount of each electrolyte component in polishing compositions can be measured in volume percent or weight percent. Volume percent refers to a percentage based on volume of a desired liquid component divided by the total volume of all of the liquid in the complete composition. A percentage based on weight percent is the weight of the desired component divided by the total weight of all of the liquid components in the complete composition. Abrading and abrasion should be broadly construed and includes, but is not limited to, contacting a material and displacing, disturbing, or removing all or a portion of a material.

[0028] The electrochemical mechanical polishing process may be performed in a process apparatus, such as a platform having one or more polishing stations adapted for electrochemical mechanical polishing processes. A platen for performing an electrochemical mechanical polishing process may include a polishing article, a first electrode, and a second electrode, wherein the substrate is in electrical contact with the second electrode. A first electrochemical mechanical polishing process may be performed on a first platen as described herein and the second electrochemical mechanical polishing process may be performed on the same or different platen adapted for electrochemical mechanical polishing, such as the second platen as described herein.

One Apparatus Embodiment

[0029] Figure 2 depicts an electrochemical processing apparatus 100 having at least two electrochemical mechanical polishing (ECMP) stations 102 and 103. Optionally, as depicted in the embodiment shown in Figure 2, the system 100 may include at least one conventional polishing station 106, such as a chemical mechanical polishing (CMP) station, disposed adjacent the ECMP station 103 on a single platform or tool. In one embodiment, polishing station 106 is a third ECMP station. One polishing tool that may be adapted to benefit from the invention is a REFLEXION® chemical mechanical polisher available from Applied Materials, Inc. located in Santa Clara, California. Examples of other polishing tools that may be

adapted to benefit from the invention are MIRRA® and MIRRA MESA™ chemical mechanical polishers also available from Applied Materials, Inc.

[0030] The exemplary apparatus 100 generally includes a base 108 that supports the ECMP stations 102 and 103, the polishing station 106, a transfer station 110 and a carousel 112. A loading robot 116 generally facilitates transfer of substrates 114 to and from the transfer station 110 of the apparatus 100 and a factory interface 120. The factory interface 120 may include a cleaning module 122, a metrology device 104 and one or more substrate storage cassettes 118. One example of a metrology device 104 that may be utilized in the factory interface 120 is a NovaScan™ Integrated Thickness Monitoring system, available from Nova Measuring Instruments, Inc., located in Phoenix, Arizona.

[0031] In one embodiment, the transfer station 110 includes an input buffer station 124, an output buffer station 126, a transfer robot 132, and a load cup assembly 128. The input buffer station 124 accepts substrates from the factory interface 120 by the loading robot 116. The loading robot 116 is also utilized to return polished substrates from the output buffer station 126 to the factory interface 120. The transfer robot 132 is utilized to move substrates between the buffer stations 124, 126 and the load cup assembly 128.

[0032] In one embodiment, the transfer robot 128 includes two gripper assemblies, each having pneumatic gripper fingers that hold the substrate 114 by the substrate's edge. The transfer robot 132 may simultaneously transfer a substrate to be processed from the input buffer station 124 to the load cup assembly 128 while transferring a processed substrate from the load cup assembly 128 to the output buffer station 126.

[0033] The carousel 112 has a plurality of arms 138, each respectively supporting one of a plurality of polishing heads 130. Each polishing head 130 retains one substrate 114 during processing. Substrates are loaded and unloaded from the polishing heads 130 by the load cup assembly 128. One of the arms 138 depicted in Figure 2 is not shown so that the transfer station 110 may be seen. The carousel 112 moves the polishing heads 130 between the load cup assembly 128 of the transfer station 110, the ECMP stations 102 and 103 and the polishing stations 106.

One carousel 112 that may be adapted to benefit from the invention is generally described in United States Patent No. 5,804,507, which is hereby incorporated by reference in its entirety. It is contemplated that other transfer mechanisms may be utilized to move substrates between the stations 102, 103, 104 and the transfer station 110.

[0034] The polishing head 130 retains the substrate 114 against the ECMP stations 102 and 103 or polishing station 106 during processing. Examples of embodiments of polishing heads 130 that may be adapted to benefit from the invention are described in United States Patent No. 6,183,354. Other polishing heads that may be adapted benefit from the invention include TITAN HEAD™ and TITAN PROFILER™ wafer carriers, available from Applied Materials, Inc. The arrangement of the ECMP stations 102 and 103 and polishing station 106 on the apparatus 100 allows for the substrate 114 to be sequentially polished by moving the substrate between stations while being retained in the same polishing head 130. Alternatively, substrates may be polished in other sequences.

[0035] To facilitate control of the polishing apparatus 100 and processes performed thereon, a controller 140 comprising a central processing unit (CPU) 142, memory 144, and support circuits 146 is connected to the polishing apparatus 100. The CPU 142 may be one of any form of computer processor that can be used in an industrial setting for controlling various drives and pressures. The memory 144 is connected to the CPU 142. The memory 144, or computer-readable medium, may be one or more of readily available memories such as random access memory (RAM), read only memory (ROM), floppy disk, hard disk, or any other form of digital storage, local or remote. The support circuits 146 are connected to the CPU 142 for supporting the processor in a conventional manner. These circuits include cache, power supplies, clock circuits, input/output circuitry, subsystems, and the like.

[0036] Figure 3 depicts one embodiment of the ECMP station 102 and/or ECMP station 103 as a cross-sectional view of one embodiment of a “face-down” process cell 200. The process cell 200 generally includes a basin 204 and a polishing head 202. A substrate 208 is retained in the polishing head 202 and lowered into the basin 204 during processing in a face down (*e.g.*, backside up) orientation. An

electrolyte, such as described herein, flows into the basin 204 and is in contact with the substrate's surface and a polishing article assembly 222, while the polishing head 202 places the substrate 208 in contact with the polishing article assembly 222. The basin 204 includes the polishing article assembly 222, a bottom 244 and sidewalls 246 that define a container that houses the polishing article assembly 222. The sidewalls 246 include a port 218 formed therethrough to allow removal of polishing composition from the basin 204. The port 218 is coupled to a valve 220 to selectively drain or retain the polishing composition in the basin 204.

[0037] The substrate 208 and the polishing article assembly 222 disposed in the basin 204 are moved relative to each other to provide a polishing motion (or motion that enhances polishing uniformity). The polishing motion generally comprises at least one motion defined by an orbital, rotary, linear or curvilinear motion, or combinations thereof, among other motions. The polishing motion may be achieved by moving either or both of the polishing head 202 and/or the basin 204. The polishing head 202 may be stationary or driven to provide at least a portion of the relative motion between the basin 204 and the substrate 208 held by the polishing head 202. In the embodiment depicted in Figure 3, the polishing head 202 is coupled to a drive system 210. The drive system 210 can generally move the polishing head 202 with at least a rotary, orbital, sweep motion, or combinations thereof.

[0038] The drive system 210 can generally move the polishing head 202 with at least a rotary, orbital, sweep motion, or combinations thereof. In one embodiment the basin 204 is rotated at a velocity from about 3 to about 100 rpm, and the polishing head 202 is rotated at a velocity from about 5 to about 200 rpm and also moved linearly at a velocity of about 5 to about 25 centimeters per second in a direction radial to the basin 204. The preferred ranges for a 200mm diameter substrate are a basin 204 rotational velocity of about 5 to about 40 rpm and a polishing head 202 rotational velocity of about 7 to about 100 rpm and a linear (e.g., radial) velocity of about 10 centimeters per second. The preferred ranges for a 300mm diameter substrate are a basin 204 rotational velocity of about 5 to about 20 rpm and a polishing head 202 rotational velocity of about 7 to about 50 rpm and a linear (e.g., radial) velocity of about 10 centimeters per second. In one embodiment

of the present invention the basin 204's diameter can range from about 17 to about 30 inches and the distance the polishing head 202 moves along the radius of the basin 204 can be from about 0.1 to about 2 inches.

[0039] The polishing head 202 generally retains the substrate 208 during processing. In one embodiment, the polishing head 202 includes a housing 214 enclosing a bladder 216. The bladder 216 may be deflated when contacting the substrate to create a vacuum therebetween, thus securing the substrate to the polishing head 202 to allow placement and removal of the substrate. The bladder 216 may additionally be inflated and pressurized to bias and assure contact between the substrate and the polishing article assembly 222 retained in the basin 204. A retaining ring 238 is coupled to the housing 214 and circumscribes the substrate 208 to prevent the substrate from slipping out from the polishing head 202 while processing. One polishing head that may be adapted to benefit from the invention is a TITAN HEAD™ carrier head available from Applied Materials, Inc., located in Santa Clara, California. Another example of a polishing head that may be adapted to benefit from the invention is described in United States Patent No. 6,159,079, issued December 12, 2001, which is hereby incorporated herein by reference in its entirety.

[0040] The basin 204 is generally fabricated from a plastic such as fluoropolymers, polytetrafluoroethylene (PTFE) polymers, such as TEFLON®, perfluoroalkoxy resin (PFA), polyethylene-based plastics (PE), sulfonated polyphenylether sulfones (PES), or other materials that are compatible or non-reactive with the polishing composition or other chemicals used in the processing cell 200. The basin 204 is rotationally supported above a base 206 by bearings 234. A drive system 236 is coupled to the basin 204 and rotates the basin 204 during processing. A catch basin 228 is disposed on the base 206 and circumscribes the basin 204 to collect processing fluids, such as a polishing composition, that flow out of port 218 disposed through the basin 204 during and/or after processing. An outlet drain 219 and outlet valve 219A are incorporated in the invention to allow the polishing composition in the catch basin to be sent to a reclaim system (not shown) or a waste drain (not shown).

[0041] In one embodiment the basin 204 is rotated at a velocity from about 3 rpm (rotations per minute) to about 100 rpm, and the polishing head 202 is rotated at a velocity from about 5 rpm to about 200 rpm and also moved linearly at a velocity from about 5 cm/s (centimeters per second) to about 25 cm/s in a direction radial to the basin 204. The preferred ranges for a 200 mm diameter substrate are a basin 204 rotational velocity from about 5 rpm to about 40 rpm and a polishing head 202 rotational velocity from about 7 rpm to about 100 rpm and a linear (*e.g.*, radial) velocity of about 10 cm/s. The preferred ranges for a 300 mm diameter substrate are a basin 204 rotational velocity from about 5 rpm to about 20 rpm and a polishing head 202 rotational velocity from about 7 rpm to about 50 rpm and a linear (*e.g.*, radial) velocity of about 10 cm/s. In one embodiment of the present invention the basin 204 has a diameter between about 17 inches (43.2 cm) and about 30 inches (76.2 cm). The polishing head 202 may move along the radius of the basin 204 for a distance between about 0.1 inches (2.5 mm) and about 2 inches (5.1 cm).

[0042] A polishing composition delivery system 232 is generally disposed adjacent the basin 204. The polishing composition delivery system 232 includes a nozzle or outlet 230 coupled to a polishing composition source 242. The outlet 230 delivers polishing composition or other processing fluids from the polishing composition source 242 into the basin 204. Alternatively, the polishing composition delivery system may provide polishing composition through an inlet (not shown) in the bottom 244 of the process cell, thus allowing polishing composition to flow through the polishing article assembly 222 to contact the conductive polishing article 203 and substrate 208. The polishing composition source 242 schematically shown here generally includes a source of all of the chemicals required to supply and support the polishing composition during processing. It is further contemplated in one embodiment of the current design to continually recirculate the polishing composition through the polishing article assembly 222 and across the surface of the substrate 208. In one embodiment the flow rate of polishing composition flowing through the process cell 200 is from about 0.1 L/min (liters per minute) to about 2 L/min.

[0043] Optionally, and shown in Figure 3, a conditioning device 250 may be provided proximate the basin 204 to periodically condition or regenerate the

polishing article assembly 222. Typically, the conditioning device 250 includes an arm 252 coupled to a stanchion 254 that is adapted to position and sweep a conditioning element 258 across polishing article assembly 222. The conditioning element 258 is coupled to the arm 252 by a shaft 256 to allow clearance between the arm 252 and sidewalls 246 of the basin 204 while the conditioning element 258 is in contact the polishing article assembly 222. The conditioning element 258 is typically a diamond or silicon carbide disk, which may be patterned to enhance working the surface of the polishing article assembly 222 into a predetermined surface condition/state that enhances process uniformity. Alternatively, the conditioning element 258 can be made of a NYLON™ brush or similar conditioner for in-situ conditioning the conductive polishing article 203. One conditioning element 258 that may be adapted to benefit from the invention is described in United States Patent Application Serial No. 09/676,280, filed September 28, 2000 by *Li et al.*, which is incorporated herein by reference to the extent not inconsistent with the claims aspects and description herein.

[0044] A power source 224 is coupled to the polishing article assembly 222 by electrical leads 223A, 223B. The power source 224 applies an electrical bias to the polishing article assembly 222 to drive an electrochemical process described below. The leads 223A, 223B are routed through a slip ring 226 disposed below the basin 204. The slip ring 226 facilitates continuous electrical connection between the power source 224 and electrodes (209 and 203) in the polishing article assembly 222 as the basin 204 rotates. The leads 223A, 223B may be wires, tapes or other conductors compatible with process fluids or having a covering or coating that protects the leads from the process fluids. Examples of materials that may be utilized in the leads 223A, 223B include copper, graphite, titanium, platinum, gold, and HASTELOY® among other materials which can have an insulating coating on its exterior surface. Coatings disposed around the leads may include polymers such as fluorocarbons, PVC, polyamide and the like. The slip ring 226 can be purchased from manufacturers such as IDM Electronics LTD, Reading Berkshire, England, a division of Kaydon Corporation, Ann Arbor, Michigan.

[0045] The polishing article assembly 222 generally includes a conductive polishing article 203, optionally coupled to a backing 207, and an electrode 209. The optional

backing 207 may also be coupled to an electrode 209. The conductive polishing article 203 and the backing 207 have a plurality of holes or pores formed therein to allow the polish composition to make contact with, and thus provide a conductive path between the substrate 208 and the electrode 209. A dielectric insert (not shown) may be disposed between the conductive polishing article 203 and the backing 207 or between the backing 207 and the electrode 209 to regulate the electrolyte flow through all or a portion of the conductive polishing article 203, by use of a plurality of holes or pores formed therein. The conductive polishing article 203 is used to apply a uniform bias to the substrate surface by use of a conductive surface that makes contact with the surface of the substrate. The use of a conductive polishing article is generally preferred over the use of a conventional substrate contacting means such as discrete or point contacts, but should not be considered limiting to the scope of the present invention. During the anodic dissolution process the electrode 209 is generally biased as a cathode and the conductive polishing article 203 and substrate are biased as an anode through use of the power supply 224.

[0046] Referring to Figure 3A, a sectional view of one embodiment of the conductive polishing article 203. The conductive polishing article 203 generally includes a conductive portion 272 adapted to contact a substrate during polishing, a sub-pad (or an article support portion) 274 and an interposed pad 276 sandwiched between the conductive portion 272 and the article support portion 274. The conductive portion 272 and article support portion 274 may be configured similar to any of the embodiments described herein or their equivalent. An optional layer of adhesive 275 may be provided on each side, with only one adhesive layer shown in Figure 3A, of the interposed pad 276 to couple the interposed pad 276 to the article support portion 274 and the conductive portion 272. The conductive portion 272, the article support portion 274 and the interposed pad 276 may be coupled by alternative methods thereby allowing the components of the conductive polishing article 203 to be easily replaced as a single unit after its service life, simplifying replacement, inventory and order management of the conductive polishing article 203.

[0047] Optionally, the support portion 274 may be coupled to an electrode 204 and replaceable with the conductive polishing article 203 as a single unit. The

conductive polishing article 203, optionally including the electrode 204, may also include a window formed therethrough.

[0048] The interposed pad 276 is generally harder than the article support portion 274 and is a hard or harder than the conductive portion 272. The invention contemplates the interposed pad 276 may alternatively be softer than the conductive portion 272. The hardness of the interposed pad 276 is selected to provide stiffness to the conductive polishing article 203, which extends the mechanical life of both the conductive portion 272 and the article support portion 274 while improving dampening characteristics of the conductive polishing article 203 resulting in greater global flatness of the polished substrate. In one embodiment, the interposed pad 276 has a hardness of less than or equal to about 80 Shore D, the article support portion 274 has a hardness of less than or equal to about 80 Shore A, while the conductive portion 272 has a hardness of less than or to about 100 Shore D. In another embodiment, the interposed pad 276 has a thickness of less than or equal to about 35 mils, while the article support portion 274 has a thickness of less than or equal to about 100 mils.

[0049] The interposed pad 276 may be fabricated from a dielectric material that permits electrical pathways to be established through the laminate comprising the conductive polishing article 203 (*i.e.*, the stack of the conductive portion 272, the interposed pad 276 and the article support portion 274). The electrical pathways may be established as the conductive polishing article 203 is immersed or covered with a conductive fluid, such as an electrolyte. To facilitate the establishment of electrical pathways through the conductive polishing article 203, the interposed pad 276 may be at least one of permeable or perforated to allow electrolyte to flow therethrough.

[0050] In one embodiment, the interposed pad 276 is fabricated from a dielectric material compatible with the electrolyte and the electrochemical process. Suitable materials include polymers, such as polyurethane, polyester, mylar sheet, epoxy and polycarbonate, among others.

[0051] A conductive backing may be disposed between the interposed pad 276 and the conductive portion 272. The conductive backing generally equalizes the

potential across the conductive portion 272, thereby enhancing polishing uniformity. Having equal potential across the polishing surface of the conductive portion 272 ensures good electrical contact between the conductive portion 272 and conductive material being polished, particularly if the conductive material is residual material that is not longer a continuous film (*i.e.*, discrete islands of film residue). Moreover, the conductive backing provides mechanical strength to the conductive portion 272, thereby increasing the service life of the conductive polishing article 203. Utilization of the conductive backing is beneficial in embodiments where the resistance through the conductive portion is greater than about 500 m-ohms and enhances the mechanical integrity of conductive portion 272. The conductive backing may also be utilized to enhance the conductive uniformity and lower the electrical resistance of the conductive portion 272.

[0052] The conductive backing may be fabricated from metal foils, metal screens, metal coated woven or non-woven fabrics among other suitable conductive materials compatible with the polishing process. The conductive backing of the conductive polishing article 203 as shown in Figure 3A comprises a conductive foil layer 1608 of a metal foil, suitable for use in an electrochemical process, such as platinum or copper, which may provide electrical contact with an electrode, and a conductive fabric 280, which may comprise a conductive material, such as copper, or a fabric coated in a conductive material, such as copper coated Nylon™ fibers, for contacting the substrate surface.

[0053] In one embodiment, the conductive backing is compression molded to the conductive portion 272. The backing is configured not to prevent the flow of electrolyte between the conductive portions 274 and the interposed pad 276. The conductive portion 272 may be mounted onto the conductive backing through compression molding, lamination, injection molding and other suitable methods.

[0054] One example of a conductive polishing article stack having a conductive polishing article 203 comprises a sub-pad 274 disposed on the electrode, the sub-pad 274 comprising a polyurethane material; an optional adhesive 275 disposed on the sub-pad 274; an interpose layer 276 disposed on the sub-pad 274, the interpose layer 276 comprising a Mylar™ material and providing mechanical strength for

subsequent layers; a conductive foil 278 disposed on the interpose layer 276, with the conductive foil 278 comprising a metal foil and providing electrical contact with an electrode; a conductive fabric 280 disposed on the conductive foil 278, with the conductive fabric 280 comprising a fabric of copper coated Nylon™ material; and a conductive polishing material 272 disposed on the conductive fabric 280 for contacting the substrate surface, with the conductive polishing material comprising a soft metal, such as Tin (Sn) disposed in a polymeric binder.

[0055] A portion or all of the conductive polishing article stack may be perforated and/or the conductive polishing material may further be grooved or embossed. The sub-pad may comprise the backing 207 above in one embodiment of the polishing article assembly 222. The conductive polishing article is more fully described in United States Patent Application No. 10/455,895, filed on June 6, 2003, of which paragraphs [0074]-[0227] are incorporated by reference herein to the extent not inconsistent with the claimed aspects and disclosure herein.

[0056] Examples of the conductive polishing articles 203 are more fully disclosed in United States Patent Publication No. 2002/0119286, filed on December 27, 2001, and United States Patent Application No. 10/211,626, filed on August 2, 2002, which are incorporated by reference herein to the extent not inconsistent with the claimed aspects and disclosure herein.

[0057] Examples of an embodiment of the conductive polishing article 203 utilizing conventional polishing material (non-conductive) with discrete conductive contacts are more fully disclosed in the United States Patent Application Serial No. 10/211,626, filed on August 2, 2003, which is incorporated by reference herein to the extent not inconsistent with the claimed aspects and disclosure herein.

[0058] As the polishing article assembly 222 includes elements comprising both an anode and cathode of an electrochemical cell, both the anode and a cathode may be replaced simultaneously by simply removing a used polishing article assembly 222 from the basin 204 and inserting a new polishing article assembly 222 with fresh electrical and supporting components into the basin 204. The face-down polishing apparatus is more fully disclosed in U.S. Patent Publication No. 20030213703, filed May 16, 2002, commonly assigned to Applied Materials Inc., of

which paragraphs 27-82 are incorporated herein by reference to the extent not inconsistent with the claims aspects and description herein.

[0059] Typically, the conductive polishing article 203, the backing 207, optionally, the dielectric insert, and the electrode 209 are secured together to form a unitary body that facilitates removal and replacement of the polishing article assembly 222 from the basin 204. The conductive polishing article 203, the backing 207, optionally the dielectric insert, and/or the electrode 209 may be coupled by use of methods such as adhesive bonding, thermal bonding, sewing, binding, heat staking, riveting, by use of fasteners and clamping, among others.

[0060] The process cell 200 may be disposed on a polishing platform with one or more chemical mechanical polishing platens suitable for conductive material and/or barrier material removal. Such chemical mechanical polishing platens may contain fixed-abrasive or non-abrasive polishing articles and may use abrasive containing or abrasive-free polishing composition. Additionally the polishing articles for the polishing platens may be hard polishing articles, having a durometer or hardness of 50 or greater on a shore D Scale or soft polishing articles having a durometer or hardness of less than 50, typically 40 or less, on a shore D Scale.

[0061] For example, the polishing platform may be of a three platen variety, such as the MIRRA® polishing system, the MIRRA MESA™ polishing system, and the REFLEXION® polishing system, that are commercially available from Applied Materials, Inc., of Santa Clara, California, with the process cell 200 disposed at a first platen position, a conventional chemical mechanical polishing platen with a hard or soft polishing pad on a second platen position, and a barrier removal platen on the third platen position. In another example, a first process cell 200 disposed at a first platen position, for example, ECMP station 102, for a first electrochemical mechanical polishing process, a second process cell 200 disposed at a second platen position, for example, ECMP station 103, for a second electrochemical mechanical polishing process, and a conventional chemical mechanical polishing platen with a hard or soft polishing pad, such as polishing station 106, on a third platen position. However, any system enabling electrochemical mechanical

polishing with or without the presence of chemical mechanical polishing ability may be used to advantage.

Polishing Processes

[0062] Methods are provided for polishing a substrate to remove residues and minimize dishing within features, while increasing throughput with a decrease in polishing time. The methods may be performed by an electrochemical polishing technique. In one aspect, the method may include processing a substrate having a conductive material layer disposed over features, supplying a first polishing composition to the surface of the substrate, applying a pressure between the substrate and a polishing article, providing relative motion between the substrate and the polishing article, applying a bias between a first electrode and a second electrode in electrical contact with the substrate, removing at least about 50% of the conductive material, supplying a second polishing composition, applying a second bias, and continuing to remove the conductive material.

[0063] One embodiment of the process will now be described in reference to Figures 4A-4D, which are schematic cross-sectional views of a substrate being processed according to methods and compositions described herein. Referring to Figure 4A, a substrate generally includes a dielectric layer 310 formed on a substrate 300. A plurality of apertures, such as vias, trenches, contacts, or holes, are patterned and etched into the dielectric layer 310, such as a dense array of narrow feature definitions 320 and low density of wide feature definitions 330. The apertures may be formed in the dielectric layer 310 by conventional photolithographic and etching techniques.

[0064] Figure 4A depicts a substrate 300 and a conductive layer 370 before ECMP processes have been applied. Figure 4B illustrates the substrate after at least about 50% of the conductive layer 370 has been removed by applying a first ECMP process. The remaining conductive layer 370 disposed upon a barrier layer 340 is removed by applying a second ECMP process, as illustrated in Figure 4C. Furthermore, as illustrated in Figure 4D, the remaining barrier layer 340 on the dielectric layer 310 may be removed by a third process, such as a CMP process or a third ECMP process.

[0065] The terms narrow and wide feature definitions may vary depending on the structures formed on the substrate surface, but can generally be characterized by the respective deposition profiles of excessive material deposition (or high overburden) formed over narrow feature definitions and minimal or low material deposition (minimal or low overburden), over wide feature definitions. For example narrow feature definitions may be about 0.13 μm in size and may have a high overburden as compared to wide feature definitions that may be about 10 μm in size and that may have minimal or insufficient overburden. However, high overburdens and low overburdens do not necessarily have to form over features, but may form over areas on the substrate surface between features.

[0066] The dielectric layer 310 may comprise one or more dielectric materials conventionally employed in the manufacture of semiconductor devices. For example, dielectric materials may include materials such as silicon dioxide, phosphorus-doped silicon glass (PSG), boron-phosphorus-doped silicon glass (BPSG), and silicon dioxide derived from tetraethyl orthosilicate (TEOS) or silane by plasma enhanced chemical vapor deposition (PECVD). The dielectric layer may also comprise low dielectric constant materials, including fluoro-silicon glass (FSG), polymers, such as polyamides, carbon-containing silicon oxides, such as BLACK DIAMOND™ dielectric material, silicon carbide materials, which may be doped with nitrogen and/or oxygen, including BLOK™ dielectric materials, available from Applied Materials, Inc. of Santa Clara, California.

[0067] A barrier layer 340 is disposed conformally in the feature definitions 320 and 330 and on the substrate 300. The barrier layer 340 may comprise metals or metal nitrides, such as tantalum, tantalum nitride, tantalum silicon nitride, titanium, titanium nitride, titanium silicon nitride, tungsten, tungsten nitride and combinations thereof, or any other material that may limit diffusion of materials between the substrate and/or dielectric materials and any subsequently deposited conductive materials.

[0068] A conductive material layer 360 is disposed on the barrier layer 340. The term "conductive material layer" as used herein is defined as any conductive material, such as copper, tungsten, aluminum, and/or their alloys used to fill a feature to form lines, contacts or vias. While not shown, a seed layer of a

conductive material may be deposited on the barrier layer prior to the deposition of the conductive material layer 360 to improve interlayer adhesion and improve subsequent deposition processes. The seed layer may be of the same material as the subsequent material to be deposited.

[0069] One type of conductive material layer 360 comprises copper containing materials. Copper containing materials include copper, copper alloys (*e.g.*, copper-based alloys containing at least about 80 weight percent copper) or doped copper. As used throughout this disclosure, the phrase "copper containing material," the word "copper," and the symbol "Cu" are intended to encompass copper, copper alloys, doped copper, and combinations thereof. Additionally, the conductive material may comprise any conductive material used in semiconductor manufacturing processing.

[0070] In one embodiment, the deposited conductive material layer 360 has a deposition profile of excessive material deposition or high overburden 370 formed over narrow feature definitions 320 and minimal overburden 380 over wide feature definitions 330. In another embodiment, high overburdens and minimal overburdens are arbitrarily formed across the substrate surface between features.

[0071] The substrate may then be positioned in a polishing apparatus, such as the apparatus descried herein and shown in Figure 3 and exposed to a polishing composition that can form a passivation layer 390 on the conductive material layer.

[0072] Alternatively, the polishing process described herein may be used to form protrusions over narrow feature definitions in the first polishing step as shown in Figures 5A-5E which are schematic cross-sections views of substrate being formed according to processes described herein. In one aspect, the method may include processing a substrate having a conductive material layer disposed over narrow feature definitions and wide feature definitions, supplying a polishing composition to the surface of the substrate, applying a pressure between the substrate and a polishing article, providing relative motion between the substrate and the polishing article, applying a bias between a first electrode and a second electrode in electrical contact with the substrate, and removing conductive material disposed over narrow

feature definitions and substrate field areas at a higher removal rate than conductive material disposed over wide feature definitions.

[0073] Figure 5A depicts a substrate 400 and a conductive layer 460 before ECMP processes have been applied. Figures 5B and 5C illustrates the substrate during removal of a first portion or bulk portion (i.e., about 50% or greater of the conductive layer) of the conductive layer 460 by applying an initial ECMP process. The removal of conductive material is selective to removing material above narrow features at higher rates than material disposed over wider features, to form a protrusion as shown in Figure 5D. The remaining conductive layer 460 disposed upon a barrier layer 440 is removed by applying a CMP process or second ECMP process, as illustrated in Figure 5E. Furthermore, the remaining barrier layer 440 on the dielectric layer 410 may be removed by a third process, such as a CMP process or a third ECMP process.

Polishing Compositions

[0074] Suitable polishing compositions that may be used with the processes described herein to planarize metals, such as copper, may comprise an acid based electrolyte system, one or more chelating agents, one or more corrosion inhibitors, one or more inorganic or organic acid salts, one or more pH adjusting agents to produce a pH between about 2 and about 10, at least one oxidizer, and abrasive particulates. In process embodiments for forming protrusion as desired in an initial ECMP process step, a composition free of abrasive particulates, free of oxidizers, or free of both, may be used.

[0075] Although the polishing compositions are particularly useful for removing copper, it is believed that the polishing compositions also may be used for the removal of other conductive materials, such as aluminum, platinum, tungsten, titanium, titanium nitride, tantalum, tantalum nitride, cobalt, gold, silver, ruthenium and combinations thereof. Mechanical abrasion, such as from contact with the conductive polishing article 203 may be used with the polishing composition to improve planarity and improve removal rate of these conductive materials.

[0076] The polishing composition includes an acid based electrolyte system for providing electrical conductivity. Suitable acid based electrolyte systems include, for example, phosphoric acid based electrolytes, sulfuric acid, nitric acid, perchloric acid, acetic acid, citric acid, salts thereof and combinations thereof. Suitable acid based electrolyte systems include an acid electrolyte, such as phosphoric acid, boric acid and/or citric acid, as well as acid electrolyte derivatives, including ammonium, potassium, sodium, calcium and copper salts thereof. The acid based electrolyte system may also buffer the composition to maintain a desired pH level for processing a substrate.

[0077] Examples of suitable acid based electrolytes include compounds having a phosphate group (PO_4^{3-}), such as, phosphoric acid, copper phosphate, potassium phosphates ($K_XH_{(3-X)}PO_4$) (x = 1, 2 or 3), such as potassium dihydrogen phosphate (KH_2PO_4), dipotassium hydrogen phosphate (K_2HPO_4), ammonium phosphates ($(NH_4)_XH_{(3-X)}PO_4$) (x = 1, 2 or 3), such as ammonium dihydrogen phosphate ($(NH_4)H_2PO_4$), diammonium hydrogen phosphate ($(NH_4)_2HPO_4$), compounds having a nitrite group (NO_3^{1-}), such as, nitric acid or copper nitrate, compounds having a boric group (BO_3^{3-}), such as, orthoboric acid (H_3BO_3) and compounds having a sulfate group (SO_4^{2-}), such as sulfuric acid (H_2SO_4), ammonium hydrogen sulfate ($(NH_4)HSO_4$), ammonium sulfate, potassium sulfate, copper sulfate, derivatives thereof and combinations thereof. The invention also contemplates that conventional electrolytes known and unknown may also be used in forming the composition described herein using the processes described herein.

[0078] The acid based electrolyte system may contains an acidic component that can take up about 1 to about 30 percent by weight (wt%) or volume (vol%) of the total composition of solution to provide suitable conductivity for practicing the processes described herein. Examples of acidic components include dihydrogen phosphate and/or diammonium hydrogen phosphate and may be present in the polishing composition in amounts from about 15 wt% to about 25 wt%. Alternately, phosphoric acid may be present in concentrations up to 30 wt%, for example, between about 2 wt% and about 6 wt%.

[0079] One aspect or component of the present invention is the use of one or more chelating agents to complex with the surface of the substrate to enhance the electrochemical dissolution process. In any of the embodiments described herein, the chelating agents can bind to a conductive material, such as copper ions, increase the removal rate of metal materials and/or improve dissolution uniformity across the substrate surface. The metal materials for removal, such as copper, may be in any oxidation state, such as 0, 1, or 2, before, during or after ligating with a functional group. The functional groups can bind the metal materials created on the substrate surface during processing and remove the metal materials from the substrate surface. The chelating agents may also be used to buffer the polishing composition to maintain a desired pH level for processing a substrate. The chelating agents may also form or enhance the formation of a passivation layer on the substrate surface.

[0080] The one or more chelating agents can include compounds having one or more functional groups selected from the group of amine groups, amide groups, carboxylate groups, dicarboxylate groups, tricarboxylate groups, hydroxyl groups, a mixture of hydroxyl and carboxylate groups, and combinations thereof. The one or more chelating agents may also include salts of the chelating agents described herein. The polishing composition may include one or more chelating agents at a concentration between about 0.1% and about 15% by volume or weight, but preferably utilized between about 0.1% and about 4% by volume or weight. For example, about 2% by volume of ethylenediamine may be used as a chelating agent.

[0081] Examples of suitable chelating agents having one or more carboxylate groups include citric acid, tartaric acid, succinic acid, oxalic acid, amino acids, salts thereof, and combinations thereof. For example, chelating agents may include ammonium citrate, potassium citrate, ammonium succinate, potassium succinate, ammonium oxalate, potassium oxalate, potassium tartrate, and combinations thereof. The salts may have multi-basic states, for example, citrates have mono-, di- and tri-basic states. Other suitable acids having one or more carboxylate groups include acetic acid, adipic acid, butyric acid, capric acid, caproic acid, caprylic acid, glutaric acid, glycolic acid, formaic acid, fumaric acid, lactic acid, lauric acid, malic

acid, maleic acid, malonic acid, myristic acid, plamitic acid, phthalic acid, propionic acid, pyruvic acid, stearic acid, valeric acid, derivatives thereof, salts thereof and combinations thereof. Further examples of suitable chelating agents include compounds having one or more amine and amide functional groups, such as ethylenediamine (EDA), diethylenetriamine, diethylenetriamine derivatives, hexadiamine, amino acids, glycine, ethylenediaminetetraacetic acid (EDTA), methylformamide, derivatives thereof, salts thereof and combinations thereof. For example, EDTA includes the acid as well as a variety of salts, such as sodium, potassium and calcium (*e.g.,* Na_2EDTA, Na_4EDTA, K_4EDTA or Ca_2EDTA).

[0082] In any of the embodiments described herein, the inorganic or organic acid salts may be used to perform as a chelating agent. The polishing composition may include one or more inorganic or organic salts at a concentration between about 0.1% and about 15% by volume or weight of the composition, for example, between about 0.1% and about 8% by volume or weight. For example, about 2% by weight of ammonium citrate may be used in the polishing composition.

[0083] Examples of suitable inorganic or organic acid salts include ammonium and potassium salts or organic acids, such as ammonium oxalate, ammonium citrate, ammonium succinate, monobasic potassium citrate, dibasic potassium citrate, tribasic potassium citrate, potassium tartarate, ammonium tartarate, potassium succinate, potassium oxalate, and combinations thereof. Additionally, ammonium and potassium salts of the carboxylate acids may also be used.

[0084] In any of the embodiments described herein, the corrosion inhibitors can be added to reduce the oxidation or corrosion of metal surfaces by forming a passivation layer that minimizes the chemical interaction between the substrate surface and the surrounding electrolyte. The layer of material formed by the corrosion inhibitors thus tends to suppress or minimize the electrochemical current from the substrate surface to limit electrochemical deposition and/or dissolution. The polishing composition may include between about 0.001% and about 5.0% by weight of the organic compound from one or more azole groups. The commonly preferred range being between about 0.2% and about 0.4% by weight.

[0085] Examples of organic compounds having azole groups include benzotriazole (BTA), mercaptobenzotriazole, 5-methyl-1-benzotriazole (TTA), and combinations thereof. Other suitable corrosion inhibitors include film forming agents that are cyclic compounds, for example, imidazole, benzimidazole, triazole, and combinations thereof. Derivatives of benzotriazole, imidazole, benzimidazole, triazole, with hydroxy, amino, imino, carboxy, mercapto, nitro and alkyl substituted groups may also be used as corrosion inhibitors. Other corrosion inhibitor includes urea and thiourea among others.

[0086] Alternatively, polymeric inhibitors, for non-limiting examples, polyalkylaryl ether phosphate or ammonium nonylphenol ethoxylate sulfate, may be used in replacement or conjunction with azole containing corrosion inhibitors in an amount between about 0.002% and about 1.0% by volume or weight of the composition.

[0087] One or more pH adjusting agents is preferably added to the polishing composition to achieve a pH between about 2 and about 10, and preferably between a pH of about 3 and about 7. The amount of pH adjusting agent can vary as the concentration of the other components is varied in different formulations, but in general the total solution may include up to about 70 wt% of the one or more pH adjusting agents, but preferably between about 0.2% and about 25% by volume. Different compounds may provide different pH levels for a given concentration, for example, the composition may include between about 0.1% and about 10% by volume of a base, such as potassium hydroxide, ammonium hydroxide, sodium hydroxide or combinations thereof, providing the desired pH level.

[0088] The one or more pH adjusting agents can be chosen from a class of organic acids, for example, carboxylic acids, such as acetic acid, citric acid, oxalic acid, phosphate-containing components including phosphoric acid, ammonium phosphates, potassium phosphates, and combinations thereof, or a combination thereof. Inorganic acids including phosphoric acid, sulfuric acid, hydrochloric, nitric acid, derivatives thereof and combinations thereof, may also be used as a pH adjusting agent in the polishing composition.

[0089] The balance or remainder of the polishing compositions described herein is a solvent, such as a polar solvent, including water, preferably deionized water. Other

solvent may be used solely or in combination with water, such as organic solvents. Organic solvents include alcohols, such as isopropyl alcohol or glycols, ethers, such as diethyl ether, furans, such as tetrahydrofuran, hydrocarbons, such as pentane or heptane, aromatic hydrocarbons, such as benzene or toluene, halogenated solvents, such as methylene chloride or carbon tetrachloride, derivatives, thereof and combinations thereof.

[0090] The polishing composition may include one or more surface finish enhancing and/or removal rate enhancing materials including abrasive particles, one or more oxidizers, and combinations thereof.

[0091] Abrasive particles may be used to improve the surface finish and removal rate of conductive materials from the substrate surface during polishing. The addition of abrasive particles to the polishing composition can allow the final polished surface to achieve a surface roughness of that comparable with a conventional CMP process even at low pad pressures. Surface finish, or surface roughness, has been shown to have an effect on device yield and post polishing surface defects. Abrasive particles may comprise up to about 30 wt% of the polishing composition during processing. A concentration between about 0.001 wt% and about 5 wt% of abrasive particles may be used in the polishing composition.

[0092] Suitable abrasive particulates particles include inorganic abrasive particulates, polymeric abrasive particulates, and combinations thereof. Inorganic abrasive particles that may be used in the electrolyte include, but are not limited to, silica, alumina, zirconium oxide, titanium oxide, cerium oxide, germania, or any other abrasive particulates of metal oxides, known or unknown. For example, colloidal silica may be positively activated, such as with an alumina modification or a silica/alumina composite. The typical abrasive particle size used in one embodiment of the current invention is generally from about 1 nm to about 1,000 nm, preferably from about 10 nm to about 100 nm. Generally, suitable inorganic abrasive particulates have a Mohs hardness of greater than 6, although the invention contemplates the use of abrasive particulates having a lower Mohs hardness value.

[0093] The polymer abrasive particulates described herein may also be referred to as "organic polymer particle abrasive particulates", "organic abrasive particulates" or "organic particles." The polymeric abrasive particulates may comprise abrasive polymeric materials. Examples of polymeric abrasive particulates materials include polymethylmethacrylate, polymethyl acrylate, polystyrene, polymethacrylonitrile, and combinations thereof.

[0094] The polymeric abrasive particulates may have a Hardness Shore D of between about 60 and about 80, but can be modified to have greater or lesser hardness value. The softer polymeric abrasive particles can help reduce friction between a polishing article and substrate and may result in a reduction in the number and the severity of scratches and other surface defects as compared to inorganic particles. A harder polymeric abrasive particle may provide improved polishing performance, removal rate and surface finish as compared to softer materials.

[0095] The hardness of the polymer abrasive particulates can be varied by controlling the extent of polymeric cross-linking in the abrasive particulates, for example, a higher degree of cross-linking produces a greater hardness of polymer and, thus, abrasive. The polymeric abrasive particulates are typically formed as spherical shaped beads having an average diameter between about 0.1 micron to about 20 microns or less.

[0096] The polymeric abrasive particulates may be modified to have functional groups, e.g., one or more functional groups, that have an affinity for, i.e., can bind to, the conductive material or conductive material ions at the surface of the substrate, thereby facilitating the ECMP removal of material from the surface of a substrate. For example, if copper is to be removed in the polishing process, the organic polymer particles can be modified to have an amine group, a carboxylate group, a pyridine group, a hydroxide group, ligands with a high affinity for copper, or combinations thereof, to bind the removed copper as substitutes for or in addition to the chemically active agents in the polishing composition, such as the chelating agents or corrosion inhibitors. The substrate surface material, such as copper, may be in any oxidation state, such as 0, 1+, or 2+, before, during or after ligating with a

functional group. The functional groups can bind to the metal material(s) on the substrate surface to help improve the uniformity and surface finish of the substrate surface.

[0097] Additionally, the polymeric abrasive particulates have desirable chemical properties, for example, the polymer abrasive particulates are stable over a broad pH range and are not prone to aggregating to each other, which allow the polymeric abrasive particulates to be used with reduced or no surfactant or no dispersing agent in the composition.

[0098] Alternatively, inorganic particles coated with the polymeric materials described herein may also be used with the polishing composition. It is within the scope of the current invention for the polishing composition to contain polymeric abrasive particulates, inorganic abrasive particulates, the polymeric coated inorganic abrasive particulates, and any combination thereof depending on the desired polishing performance and results.

[0099] One or more oxidizers may be used herein to enhance the removal or removal rate of the conductive material from the substrate surface. An oxidizing agent is generally an agent that reacts with a material by accepting an electron(s). In the current embodiment the oxidizer is used to react with the surface of the substrate that is to be polished, which then aids in the removal of the desired material. For example, an oxidizer may be used to oxidize a metal layer to a corresponding oxide or hydroxide, for example, copper to copper oxide. Existing copper that has been oxidized, including Cu1+ ions, may further be oxidized to a higher oxidation state, such as Cu2+ ions, which may then promote the reaction with one or more of the chelating agents. Also, in some instances the oxidizing agent can be used in some chemistries (e.g., low pH) that can enhance the chemical etching of the surface of the substrate to further increase the removal rate from the anode surface. In cases where no bias is applied to the surface of the substrate the inhibitors and chelating agents will complex with the metal ions on the surface that become dislodged from the surface due to the relative motion and pressure applied by the conductive pad 203. The addition of abrasive particulates can further improve the removal rate of the complexed metal ions due to the

abrasive particles ability to increase that contact area between the conductive pad 203 and the substrate surface.

[0100] In the case of ECMP, the conductive layer on the substrate surface is biased anodically above a threshold potential, by use of the power source 224 and the electrode 209, thus causing the metal on the substrate surface to "oxidize" (i.e., a metal atom gives up one or more electrons to the power source 224). The ionized or "oxidized" metal atoms thus dissolve into the electrolyte solution with the help of components in the electrolyte. In the case where copper is the desired material to be removed, it can be oxidized to a Cu1+ or a Cu2+ oxidation state. Due to the presence of the inhibitors and/or chelating agents found in the polishing composition, the electrochemical dissolution process of the metal ions into the electrolyte is more limited than a polishing composition which does not contain these components. The presence of the inhibitors and/or chelating agents also appears to have an effect on the attachment strength of the metal ion(s) and inhibitor and/or chelating agent complex to the surface of the substrate. It has been found that in one embodiment that the removal rate in an ECMP process can be increased by the addition of an oxidizing agent. It is thought that the oxidizing agent tends to further oxidize the metal ions formed due to the anodic bias, which in the case of copper brings it to the more stable Cu2+ oxidation state. The inhibitors and/or chelating agents found in the polishing composition complex with the oxidized metal ions which tend to have a lower attachment, or bond, strength due to the way the inhibitor bonds to the oxidized metal ion and metal surface. The lower attachment strength allows the complexed metal ion to be more easily and efficiently removed due to the interaction of the substrate surface and the conductive pad 203. The addition of abrasive particulates to the ECMP polishing composition can further improve the removal rate of the complexed metal ions due to the abrasive particles' ability to increase contact area between the conductive pad 203 and the substrate surface.

[0101] The polishing composition may include one or more additive compounds. Additive compounds include electrolyte additives including, but not limited to, suppressors, enhancers, levelers, brighteners, stabilizers, and stripping agents to improve the effectiveness of the polishing composition in polishing of the substrate

surface. For example, certain additives may decrease the ionization rate of the metal atoms, thereby inhibiting the dissolution process, whereas other additives may provide a finished, shiny substrate surface. The additives may be present in the polishing composition in concentrations up to about 15% by weight or volume, and may vary based upon the desired result after polishing.

[0102] Further, controlling the amounts and types of constituents of the polishing composition, such as corrosion inhibitors and oxidizers, can result in tuning the desired removal rate of the process. For example reduced amounts of corrosion inhibitor will result in an increase in the material removal rate as compared to compositions having higher corrosion inhibitor concentrations. In cases where the polishing composition does not contain corrosion inhibitors the ECMP material removal rate is greatly increased over a polishing composition which contains a corrosion inhibitor due to the formation of the metal ions and inhibitor complex which tends to shield the surface of the substrate to the electrolyte. Likewise reduced amounts of oxidizers will generally result in lower removal rates compared to compositions having higher oxidizer compositions. It has been suggested that at low concentrations of the oxidizer, the corrosion inhibitor and/or chelating agent can complex with a metal ion before it becomes oxidized further by the oxidizing agent due to kinetic effects limiting the supply of the oxidizer to the surface of the substrate. The corrosion inhibitor and metal ion complex can thus affect the removal efficiency due to the formation of the stronger attachment strength complexed metal ions. An example of a polishing composition described herein includes about 2% by volume ethylenediamine, about 2% by weight ammonium citrate, about 0.3% by weight benzotriazole, between about 0.1% and about 3% by volume or weight, for example, about 0.45% hydrogen peroxide, and/or about between about 0.01% and 1% by weight, for example 0.15% by weight, of abrasive particles, and about 6% by volume phosphoric acid. The pH of the composition is about 5, which may be achieved by, for example, the composition further including potassium hydroxide to adjust the pH to the preferred range. The remainder of the polishing composition is deionized water.

[0103] The oxidizer can be present in the polishing composition in an amount ranging between about 0.01% and about 90% by volume or weight, for example,

between about 0.1% and about 20% by volume or weight. In an embodiment of the polishing composition, between about 0.1% to about 15% by volume or weight of hydrogen peroxide is present in the polishing composition. In one embodiment, the oxidizer is added to the rest of the polishing composition just prior to beginning the ECMP process. Examples of suitable oxidizers include peroxy compounds, e.g., compounds that may disassociate through hydroxy radicals, such as hydrogen peroxide and its adducts including urea hydrogen peroxide, percarbonates, and organic peroxides including, for example, alkyl peroxides, cyclical or aryl peroxides, benzoyl peroxide, peracetic acid, and ditertbutyl peroxide. Sulfates and sulfate derivatives, such as monopersulfates and dipersulfates may also be used including for example, ammonium peroxydisulfate, potassium peroxydisulfate, ammonium persulfate, and potassium persulfate. Salts of peroxy compounds, such as sodium percarbonate and sodium peroxide may also be used.

[0104] The oxidizing agent can also be an inorganic compound or a compound containing an element in its highest oxidation state. Examples of inorganic compounds and compounds containing an element in its highest oxidation state include but are not limited to periodic acid, periodate salts, perbromic acid, perbromate salts, perchloric acid, perchloric salts, perbonic acid, nitrate salts (such as cerium nitrate, iron nitrate, ammonium nitrate), ferrates, perborate salts and permanganates. Other oxidizing agents include bromates, chlorates, chromates, iodates, iodic acid, and cerium (IV) compounds such as ammonium cerium nitrate.

[0105] Surfactants may be one such additive compound in the polishing composition. One or more surfactants may be used in the polishing composition to increase the dissolution or solubility of materials, such as metals and metal ions or by-products produced during processing, improve chemical stability, and reduce decomposition of components of the polishing composition. The one or more surfactants can comprise a concentration between about 0.001% and about 10% by volume or weight of the polishing composition. A concentration between about 0.01% and about 2% by volume or weight, for example between about 0.1% and about 1% by volume or weight, of the surfactants may be used in one embodiment of the polishing composition. The one or more surfactants may include non-ionic surfactants as well as ionic surfactants including anionic surfactants, cationic

surfactants, amphoteric surfactants, and ionic surfactants having more than one ionic functional group, such as Zweitter-ionic surfactants. Dispersers or dispersing agents are considered to be surfactants as surfactants are used herein.

[0106] Other examples of additives include one or more leveling agents, which are broadly defined herein as additives that suppress dissolution current on the surface of a substrate. Leveling agents suppress dissolution current by attaching to conductive materials, by inhibiting the electrochemical reactions between the electrolyte and conductive material, and/or form depolarizing agents that limit electrochemical reactions. A concentration of leveling agents between about 0.005% and about 10% by volume or weight, for example, between about 0.05% and about 2% by volume or weight of the electrolyte solution can be used.

[0107] Leveling agents include, but are not limited to, polyethylene glycol (PEG) and polyethylene glycol derivatives. Other leveling agents which can be employed in the process described herein include any employed in the electroplating or electropolishing art, such as polyamines, polyamides and polyimides including polyethyleneimine, polyglycine, 2-amino-1-naphthalenesulfonic acid, 3-amino-1-propanesulfonic acid, 4-aminotoluene-2-sulfonic acid. Leveling agents may be added to the composition in a range from about 0.05% to about 5% by volume or weight of the composition. For example, PEG may be added to a polishing solution with a concentration about 0.2 wt%.

[0108] Suppressors, such as electrically resistive additives that reduce the conductivity of the polishing composition may be added to the composition in a range from about 0.005% to about 2% by volume or weight of the composition. Suppressors include polyacrylamide, polyacrylic acid polymers, polycarboxylate copolymers, coconut diethanolamide, oleic diethanolamide, ethanolamide derivatives, or combinations thereof.

[0109] One or more stabilizers may be present in an amount that is sufficient to produce measurable improvements in composition stability. The one or more stabilizers may be present in an amount ranging from about 100 ppm to about 5.0 weight percent (wt%). Non-limiting examples of preferred stabilizers include but are not limited to phosphoric acids and phosphoric acid derivatives including

aminotri(methylenephosphonic) acid, 1-hydroxyethylidene-4-diphosphonic acid, hexamethylenediaminetetramethylene phosphoric acid, and diethylenetetramine pentamethylenephosphonic acid, and derivative salts thereof.

[0110] Accelerators are another example of an additive that may be included in the polishing composition. Accelerators increase electrochemical reactions of metals disposed on the substrate surface to increase metal removal. The composition may include one or more accelerators at a concentration between about 0.001% and about 1% by volume or weight, for example, between about 0.25% and about 0.8% by volume or weight. Accelerators may include sulfur-containing compounds, such as sulfite or di-sulfate.

[0111] Further examples of additives to the polishing composition are more fully described in United States Patent Application No. 10/141,459, filed on May 7, 2002, which is incorporated by reference herein to the extent not inconsistent with the claimed aspects and disclosure herein.

[0112] ECMP solutions of varying compositions may be used to remove bulk material and residual material, such as copper and/or copper alloys, as well as to remove barrier materials, such as tantalum nitrides or titanium nitrides. Specific formulations of the polishing compositions are used to remove the particular materials. Polishing compositions utilized during embodiments herein are advantageous for ECMP processes. Generally, ECMP solutions are much more conductive than traditional CMP solutions. The ECMP solutions have a conductivity of about 10 mS or higher, while traditional CMP solutions have a conductivity from about 3 mS to about 5 mS. The conductivity of the ECMP solutions greatly influences that rate at which the ECMP process advances, i.e., more conductive solutions have a faster material removal rate. For removing bulk material, the ECMP solution has a conductivity of about 10 mS or higher, preferably in a range from about 30 mS to about 60 mS. For residual material, the ECMP solution has a conductivity of about 10 mS or higher, preferably in a range from about 15 mS to about 40 mS.

[0113] A first polishing composition or first ECPM solution used to remove bulk material may include phosphoric acid, at least one chelating agent, a corrosion

inhibitor, a salt, an oxidizer, or abrasive particulates. For example, a first polishing solution may include from about 1 wt% to about 10 wt% of phosphoric acid; from about 0.1 wt% to about 6 wt% of the at least one chelating agent; from about 0.01 wt% to about 1 wt% of a corrosion inhibitor; from about 0.5 wt% to about 10 wt% of a salt, such as ammonium citrate or copper citrate; from about 0.2 wt% to about 5 wt% of an oxidizer; and from about 0.05 wt% to about 1 wt% of abrasive particulates. Also, a first polishing composition may have a pH adjusting agent in a concentration to maintain a pH from about 4 to about 7. Generally, a solvent is added to the solution, such as de-ionized water.

[0114] The first polishing composition includes at least one chelating agent, such as EDA, EDTA, citric acid, ammonium citrate, salts thereof, derivatives thereof and combinations thereof. The corrosion inhibitor of the first polishing composition may include BTA, TTA, salts thereof, derivatives thereof and combinations thereof. Salts may be added to the first polishing composition or may be formed in situ, such as by an acid/base type reaction. Salts may be inorganic, organic or combinations thereof and include cations such as ammonium, potassium, sodium, calcium and anions such as citrate, oxalate, succinate and tartrate. A pH adjusting agent includes potassium hydroxide, ammonium hydroxide or combinations thereof. An oxidizer, such as hydrogen peroxide and/or abrasive particulates, such as colloidal silica activated with alumina may be added to the first polishing composition.

[0115] A second polishing composition or second ECPM solution used to residual material may include phosphoric acid, at least one chelating agent, a corrosion inhibitor, a salt, an oxidizer, abrasive particulates. For example, a second polishing solution may include from about 0.1 wt% to about 5 wt% of phosphoric acid; from about 0.1 wt% to about 5 wt% of the at least one chelating agent; from about 0.01 wt% to about 1 wt% of a corrosion inhibitor; from about 0.1 wt% to about 5 wt% of a salt; from about 0.01 wt% to about 3 wt% of an oxidizer; and from about 0.05 wt% to about 5 wt% of abrasive particulates. Also, a second polishing composition may have a pH adjusting agent in a concentration to maintain a pH from about 4 to about 7. Generally, a solvent is added to the solution, such as de-ionized water.

[0116] The at least one chelating agent of the second polishing composition may include glycine, EDA, EDTA, citric acid, ammonium citrate, salts thereof, derivatives thereof and combinations thereof. The corrosion inhibitor of the second polishing composition may include BTA, TTA, salts thereof, derivatives thereof and combinations thereof. Salts may be added to the second polishing composition or may be formed in situ, such as by an acid/base type reaction. Salts may be inorganic, organic or combinations thereof and include cations such as ammonium, potassium, sodium, calcium and anions such as citrate, oxalate, succinate and tartrate. A pH adjusting agent includes potassium hydroxide, ammonium hydroxide or combinations thereof. An oxidizer, such as hydrogen peroxide and/or abrasive particulates, such as colloidal silica activated with alumina may be added to the second polishing composition. In one example, a second polishing composition includes BTA and glycine. In another example, a second polishing composition includes BTA, EDA and ammonium citrate. Also, some of the second polishing compositions contain leveling agents, such as PEG.

<u>**Electrochemical Mechanical Processing:**</u>

[0117] An electrochemical mechanical polishing technique using a combination of chemical activity, mechanical activity and electrical activity to remove material and planarize a substrate surface may be performed as follows. In one embodiment of an electrochemical mechanical polishing technique, the substrate is disposed in a receptacle, such as a basin or platen containing a first electrode and a polishing composition. The polishing composition forms a passivation layer on the substrate surface. The passivation layer may chemically and/or electrically insulate material disposed on a substrate surface.

[0118] A polishing article coupled to a polishing article assembly containing a second electrode is then disposed in the basin or platen and physically contacted and/or electrically coupled with the substrate through the polishing article. Relative motion is provided between the substrate surface and the conductive article 203 to reduce or remove the passivation layer. A bias from a power source 224 is applied between the two electrodes. The bias may be applied by an electrical pulse modulation technique providing at least anodic dissolution. The bias may be

transferred from a conductive article 203 in the polishing article assembly 222 to the substrate 208.

[0119] A first ECMP process may be used to remove bulk conductive material from the substrate surface as shown from Figures 4A-4B and then a second ECMP process to remove residual copper containing materials as shown from Figures 4B-4C. Bulk material is broadly defined herein as any material deposited on the substrate in an amount more than sufficient to substantially fill features formed on the substrate surface. Residual material is broadly defined as any bulk copper containing material remaining after one or more polishing process steps. Generally, the bulk removal during a first ECMP process removes at least about 50% of the conductive layer, preferably at least about 70%, more preferably at least about 80%, for example, at least about 90%. The residual removal during a second ECMP process removes most, if not all the remaining conductive material disposed on the barrier layer to leave behind the filled plugs.

[0120] The first ECMP process attributes to the throughput of substrate manufacturing due to a fast removal rate of the conductive layer. However, if the first ECMP process is used solely, too much conductive material may be removed to produce an under burden. The second ECMP process attributes to the throughput of substrate manufacturing due to the precise removal the conductive layer to form level substrate surfaces. However, the second ECMP process is too slow are removing conducting material to be solely used. Therefore, the combined first and second ECMP processes increases throughput and produces high quality planar substrate surfaces.

[0121] The bulk removal ECMP process may be performed on a first polishing platen and the residual removal ECMP process on a second polishing platen of the same or different polishing apparatus as the first platen. In another embodiment, the residual removal ECMP process may be performed on the first platen. Any barrier material may be removed on a separate platen, such as the third platen in the apparatus described in Figure 2. For example, the apparatus described above in accordance with the processes described herein may include three platens for removing bulk material or comprise one platen to remove bulk material, a second

platen for residual removal and a third platen for barrier removal, wherein the bulk and the residual processes are ECMP processes and the barrier removal is a CMP process. In another embodiment, three ECMP platens may be used to remove bulk material, residual removal and barrier removal.

[0122] Referring to Figures 4A-4B, the substrate 300 having a dielectric layer 310 patterned with narrow feature definitions 320 and wide feature definitions 330 is filled with a barrier layer 340, for example, tantalum, and an excess amount of conductive material 360, for example, copper. The deposition profile of the excess material includes a high overburden 370, also referred to as a hill or peak, formed over narrow feature definitions 320 and a minimal overburden 380, also referred to as a valley, over wide feature definitions 330.

[0123] The substrate is exposed to a polishing composition described herein that forms a passivation layer 390 on the conductive material layer 360. The passivation layer 390 forms on the exposed conductive material 360 on the substrate surface including the high overburden 370, peaks, and minimal overburden 380, valleys, formed in the deposited conductive material 360. The passivation layer 390 chemically and/or electrically insulates the surface of the substrate from chemical and/or electrical reactions. The passivation layer is formed from the exposure of the substrate surface to the corrosion inhibitor and/or other materials capable of forming a passivating or insulating film, for example, chelating agents. The thickness and density of the passivation layer can dictate the extent of chemical reactions and/or amount of anodic dissolution. For example, a thicker or denser passivation layer 390 has been observed to result in less anodic dissolution compared to thinner and less dense passivation layers. Thus, control of the composition of passivating agents, corrosion inhibitors and/or chelating agents, allow control of the removal rate and amount of material removed from the substrate surface.

[0124] Figure 4B illustrates that at least about 50% of the conductive material 360 was removed after the bulk removal of the first ECMP process, for example, about 90%. After the first ECMP process, conductive material 360 may still include the high overburden 370, peaks, and/or minimal overburden 380, valleys, but with a

reduced proportionally size. However, conductive material 360 may also be rather planar across the substrate surface (not pictured).

[0125] The substrate surface and a polishing article, such as conductive polishing article, are contacted with one another and moved in relative motion to one another, such as in a relative orbital motion, to remove portions of the passivation layer 390 formed on the exposed conductive material 360, which may also remove a portion of the underlying conductive material 360.

[0126] The substrate surface and polishing article are contacted at a pressure less than about 2 pounds per square inch (lb/in2 or psi) (13.8 kPa). Removal of the passivation layer 390 and some conductive material 360 may be performed with a process having a pressure of about 1 psi (6.9 kPa) or less, for example, from about 0.01 psi (69 Pa) to about 0.5 psi (3.4 kPa). In one aspect of the process, a pressure of about 0.2 psi (1.4 kPa) or less is used.

[0127] The polishing pressures used herein reduce or minimize damaging shear forces and frictional forces for substrates containing low k dielectric materials. Reduced or minimized forces can result in reduced or minimal deformations and defect formation of features from polishing. Further, the lower shear forces and frictional forces have been observed to reduce or minimize formation of topographical defects, such as dishing and scratches, and delamination, during polishing. Contact between the substrate and a conductive polishing article also allows for electrical contact between the power source and the substrate by coupling the power source to the polishing article when contacting the substrate. A region of non-passivated material may be exposed and removed by anodic dissolution by mechanical abrasion to disturb or remove the passivation layer on the surface of the substrate.

[0128] A bias is applied to the substrate during contact between the substrate surface and the conductive polishing article for anodic dissolution of the conductive material 360 from the substrate surface. The bias is generally provided to produce anodic dissolution of the conductive material from the surface of the substrate at a current density up to about 100 mA/cm2 which correlates to an applied current of about 40 amps to process substrates with a diameter up to about 300 mm. For

example, a 300 mm diameter substrate may have a current density from about 0.001 mA/cm2 to about 50 mA/cm2, which correlates to an applied current from about 0.01 A to about 35 A. The invention also contemplates that the bias may be applied and monitored by volts, amps and watts. For example, in one embodiment, the power supply may apply a power between about 0 watts and 100 watts, a voltage between about 0 V and about 10 V, and a current between about 0 amps and about 10 amps.

[0129] During anodic dissolution under application of the bias, the substrate surface, i.e., the conductive material layer 360 may be biased anodically above a threshold potential of the conductive material, for example, a metal material, on the substrate surface to "oxidize". When a metal material oxidizes, a metal atom gives up one or more electrons to the power source and forms metal ions or cations. The metal ions may then leave the substrate surface and dissolve into the electrolyte solution. In the case where copper is the desired material to be removed, cations can have the Cu1+ or Cu2+ oxidation state.

[0130] The metal ions may also contribute to the formation of the thickness and/or density of the passivation layer 390. For example, the inhibitors and/or chelating agents found in the polishing composition may complex with the metal ions and the metal ions become incorporated into the passivation layer 390. Thus, the presence of the inhibitors and/or chelating agents found in the polishing composition limit or reduce the electrochemical dissolution process of the metal ions into the electrolyte, and further incorporate such metal ions into the passivation layer 390. It has been observed that the thickness and/or density of the undisturbed passivation layer may increase after periods of applied bias for anodic dissolution of conductive materials on the substrate surface. It is believed that the increase in the thickness and/or density of the undisturbed passivation layer is related to the total applied power and is a function of time and/or power levels. It has also been observed that the undisturbed passivation layer incorporates metal ions and that the metal ions may contribute to the thickness and/or density of the passivation layer.

[0131] The bias may be varied in power and application depending upon the user requirements in removing material from the substrate surface. For example,

increasing power application has been observed to result in increasing anodic dissolution. The bias may also be applied by an electrical pulse modulation technique. Pulse modulation techniques may vary, but generally include a cycle of applying a constant current density or voltage for a first time period, then applying no current density or voltage or a constant reverse current density or voltage for a second time period. The process may then be repeated for one or more cycles, which may have varying power levels and durations. The power levels, the duration of power, an "on" cycle, and no power, an "off" cycle" application, and frequency of cycles, may be modified based on the removal rate, materials to be removed, and the extent of the polishing process. For example, increased power levels and increased duration of power being applied have been observed to increase anodic dissolution.

[0132] In one pulse modulation process for electrochemical mechanical polishing, the pulse modulation process comprises an on/off power technique with a period of power application, "on", followed by a period of no power application, "off". The on/off cycle may be repeated one or more times during the polishing process. The "on" periods allow for removal of exposed conductive material from the substrate surface and the "off" periods allow for polishing composition components and by-products of "on" periods, such as metal ions, to diffuse to the surface and complex with the conductive material. During a pulse modulation technique process it is believed that the metal ions migrate and interact with the corrosion inhibitors and/or chelating agents by attaching to the passivation layer in the non-mechanically disturbed areas. The process thus allows etching in the electrochemically active regions, not covered by the passivation layer, during an "on" application, and then allowing reformation of the passivation layer in some regions and removal of excess material during an "off" portion of the pulse modulation technique in other regions. Thus, control of the pulse modulation technique can control the removal rate and amount of material removed from the substrate surface.

[0133] The "on"/"off" period of time may be between about 1 second and about 60 seconds each, for example, between about 2 seconds and about 25 seconds, and the invention contemplates the use of pulse techniques having "on" and "off" periods of time greater and shorter than the described time periods herein. In one example

of a pulse modulation technique, power is applied between about 16% and about 66% of each cycle.

[0134] Non-limiting examples of pulse modulation technique with an on/off cycle for electrochemical mechanical polishing of materials described herein include: applying power, "on", between about 5 seconds and about 10 seconds and then not applying power, "off", between about 2 seconds and about 25 seconds; applying power for about 10 seconds and not applying power for 5 seconds, or applying power for 10 seconds and not applying power for 2 seconds, or even applying power for 5 seconds and not applying power for 25 seconds to provide the desired polishing results. The cycles may be repeated as often as desired for each selected process. One example of a pulse modulation process is described in commonly assigned United States Patent Number 6,379,223, which is incorporated by reference herein to the extent not inconsistent with the claimed aspects and disclosure herein. Further examples of a pulse modulation process is described in co-pending United States Provisional Patent Application Serial No. 10/611,805, entitled "Effective Method To Improve Surface Finish In Electrochemically Assisted Chemical Mechanical Polishing", filed on June 30, 2003, which is incorporated by reference herein to the extent not inconsistent with the claimed aspects and disclosure herein.

[0135] Power application may also vary on processing steps. For example, in a two step process the first processing step may have a first application of power, and a second step may have a second application of power less than the first application of power. Conversely, in a two step process the first processing step may have a first application of power, and a second step may have a second application of power greater than the first application of power.

[0136] A removal rate of conductive material of up to about 15,000 Å/min can be achieved by the processes described herein. Higher removal rates are generally desirable, but due to the goal of maximizing process uniformity and other process variables (e.g., reaction kinetics at the anode and cathode) it is common for dissolution rates to be controlled from about 100 Å/min to about 15,000 Å/min. In one embodiment of the invention where the copper material to be removed is less

than 5,000 Å thick, the voltage (or current) may be applied to provide a removal rate from about 100 Å/min to about 5,000 Å/min. The substrate is typically exposed to the polishing composition and power application for a period of time sufficient to remove at least a portion or all of the desired material disposed thereon.

[0137] The polishing composition may be varied to control the rate in which the conductive material is removed. In one embodiment, a first ECMP process is conducted with a first polishing solution, thereafter, a second ECMP process is conducted with a second polishing solution more dilute than the first polishing solution, for example, the second polishing solution is about 25% the concentration of the first polishing solution. For example, the first ECMP composition may comprise: from about 1 wt% to about 10 wt% of phosphoric acid; from about 0.1 wt% to about 6 wt% of the at least one chelating agent; from about 0.01 wt% to about 1 wt% of the corrosion inhibitor; from about 0.5 wt% to about 10 wt% of the salt; from about 0.2 wt% to about 5 wt% of the oxidizer; and from about 0.05 wt% to about 1 wt% of the abrasive particulates. The second ECMP composition may comprise: from about 0.25 wt% to about 5 wt% of phosphoric acid; from about 0.05 wt% to about 3 wt% of the at least one chelating agent; from about 0.005 wt% to about 0.5 wt% of the corrosion inhibitor; from about 0.13 wt% to about 5 wt% of the salt; from about 0.05 wt% to about 3 wt% of the oxidizer; andfrom about 0.02 wt% to about 0.5 wt% of the abrasive particulates. In some embodiments, the first ECMP solution and second ECMP solution have the similar relative concentrations of each component except water, whereas the second ECMP solution is formed by combining de-ionized water to the first ECMP solution, for example at a volume ratio of about 3 to about 1. In other embodiments, the first polishing solution and second polishing solution have the varied relative concentrations of each component within water.

[0138] Generally, the removal rate of conductive material 360 is much faster during the first ECMP process than during the second ECMP process. For example, the first ECMP process removes conductive material 360 at a rate from about 1,000 Å/min to about 15,000 Å/min, while the second ECMP process removes conductive material 360 at a rate from about 100 Å/min to about 8,000 Å/min. The second ECMP process is slower in order to prevent excess metal removal to form

topographical defects, such as concavities or depressions known as dishing 55, as shown in Figure 1B. Therefore, a majority of the conductive layer 360 is removed at a faster rate during the first ECMP process than the remaining conductive layer 360 during the second ECMP process. The two-step ECMP process increases throughput of the total substrate processing and while producing a smooth surface with little or no defects.

[0139] Mechanical abrasion by a conductive polishing article removes the passivation layer that insulates or suppresses the current for anodic dissolution, such that areas of high overburden is preferentially removed over areas of minimal overburden as the passivation layer is retained in areas of minimal or no contact with the conductive polishing article 203. The removal rate of the conductive material 360 covered by the passivation layer is less than the removal rate of conductive material without the passivation layer. As such, the excess material disposed over narrow feature definitions 320 and the substrate field 350 is removed at a higher rate than over wide feature definitions 330 still covered by the passivation layer 390.

[0140] Referring to Figure 4C, most, if not all of the conductive layer 360 is removed to expose barrier layer 340 and conductive trenches 365 by polishing the substrate with a second ECMP process including a second ECMP polishing solution. The conductive trenches 365 are formed by the remaining conductive material 360. Any residual conductive material and barrier material may then be polished by a third polishing step to provide a planarized substrate surface containing conductive trenches 365, as depicted in Figure 4D. The residual conductive material and barrier material may be removed by a third polishing process, such as a third ECMP process or a CMP process. An example of a copper polishing process is disclosed in United States Patent Publication Number 20030029841 and an example of a barrier polishing process is disclosed in United States Patent Publication Number 20030013306, which are both incorporated herein to the extent not inconsistent with the claims aspects and disclosure herein.

[0141] After conductive material and barrier material removal processing steps, the substrate may then be buffed to minimize surface defects. Buffing may be

performed with a soft polishing article, i.e., a hardness of about 40 or less on the Shore D hardness scale as described and measured by the American Society for Testing and Materials (ASTM), headquartered in Philadelphia, Pennsylvania, at reduced polishing pressures, such as about 2 psi or less. An example of a suitable buffing process and composition is disclosed in co-pending United States Patent Application Serial No. 09/569,968, filed on May 11, 2000, and incorporated herein by reference to the extent not inconsistent with the invention.

[0142] Optionally, a cleaning solution may be applied to the substrate after each of the polishing process to remove particulate matter and spent reagents from the polishing process as well as help minimize metal residue deposition on the polishing articles and defects formed on a substrate surface. An example of a suitable cleaning solution is ElectraClean™ commercially available from Applied Materials, Inc., of Santa Clara, California.

[0143] Finally, the substrate may be exposed to a post polishing cleaning process to reduce defects formed during polishing or substrate handling. Such processes can minimize undesired oxidation or other defects in copper features formed on a substrate surface. An example of such a post polishing cleaning is the application of Electra Clean™, commercially available from Applied Materials, Inc., of Santa Clara, California.

[0144] It has been observed that substrate planarized by the processes described herein have exhibited reduced topographical defects, such as dishing, reduced residues, improved planarity, and improved substrate finish. The processes described herein may be further disclosed by the examples as follows.

<u>Electrochemical Mechanical Protrusion Processing:</u>

[0145] Alternatively, an electrochemical mechanical polishing technique using a combination of chemical activity, mechanical activity, and electrical activity to remove material and planarize a substrate surface with an intermediate protrusion formation may be performed as follows.

[0146] The electrochemical polishing process may be used to remove bulk conductive material from the substrate surface as shown in Figures 5A-5C and then

chemical mechanical polishing or a second electrochemical polishing process to remove residual copper containing materials as shown in Figures 5D-5E. Bulk material is broadly defined herein as any material deposited on the substrate in an amount more than sufficient to substantially fill features formed on the substrate surface. Residual material is broadly defined as any bulk copper containing material remaining after one or more polishing process steps.

[0147] The bulk removal electrochemical mechanical polishing process may be performed on a first polishing platen and the residual removing process on a second polishing platen of the same or different polishing apparatus as the first platen. Any barrier material used to prevent conductive material diffusion through layer of a substrate may be removed on a separate platen, such as the third platen in the apparatus described herein. For example, the apparatus described above in accordance with the processes described herein may include three platens for removing bulk material or comprise one platen to remove bulk material, a second platen for residual removal, and a third platen for barrier removal.

[0148] Referring to Figure 5A, the substrate 400 having a dielectric layer 410 patterned with narrow feature definitions 420 and wide feature definitions 430 is field with a barrier layer 440, for example, tantalum, and an excess amount of conductive material 460, for example, copper. The deposition profile of the excess material includes a high overburden 470, also referred to as a hill or peak, formed over narrow feature definitions 420 and a minimal overburden 480, also referred to as a valley, over wide feature definitions 430.

[0149] The substrate is exposed to a polishing composition 495 described herein that forms a passivation layer 490 on the conductive material layer 460. The passivation layer 490 forms on the exposed conductive material 460 on the substrate surface including the high overburden 470, peaks, and minimal overburden 480, valleys, formed in the deposited conductive material 460. The passivation layer 490 chemically and/or electrically insulates the surface of the substrate from chemical and/or electrical reactions. The passivation layer is formed from the exposure of the substrate surface to the corrosion inhibitor and/or other materials capable of forming a passivating or insulating film, for example, chelating

agents. The thickness and density of the passivation layer can dictate the extent of chemical reactions and/or amount of anodic dissolution. For example, a thicker or denser passivation layer 490 has been observed to result in less anodic dissolution compared to thinner and less dense passivation layers. Thus, control of the composition of passivating agents, corrosion inhibitors and/or chelating agents, allow control of the removal rate and amount of material removed from the substrate surface.

[0150] The substrate surface and a polishing article, such as conductive polishing article 203, are contacted with one another and moved in relative motion to one another, such as in a relative orbital motion, to remove portions of the passivation layer 490 formed on the exposed conductive material 460 as shown in Figure 5B, which may also remove a portion of the underlying conductive material 460.

[0151] The substrate surface and polishing article are contacted at a pressure less than about 2 psi. Removal of the passivation layer 490 and some conductive material 460 may be performed with a process having a pressure of about 1 psi or less, for example, between about 0.01 psi and about 0.5 psi. In one aspect of the process, a pressure of about 0.2 psi or less is used.

[0152] Referring to Figure 5C, mechanical abrasion by the conductive polishing article 203 removes the passivation layer that insulates or suppresses the current for anodic dissolution, such that areas of high overburden 470 and the substrate field 450 are preferentially removed over areas of minimal overburden 480 as the passivation layer is retained in areas of minimal or no contact with the conductive polishing article 203. The removal rate of the conductive material 460 covered by the passivation layer is less than the removal rate of conductive material without the passivation layer. As such, the excess material disposed over narrow feature definitions 420 and the substrate field 450 is removed at a higher rate than over wide feature definitions 430 still covered by the passivation layer 490.

[0153] Referring to Figure 5D, the process described herein may allow for the formation of a protrusion 500 in the conductive material layer 460 formed over the wide features. The protrusion 500 is formed from material that was unpolished or polished at a reduced removal rate due to the formation of a thicker or more dense

passivation layer or for longer durations than other portions of the conductive material layer 460. For example, the protrusion may be up to about 50% of the deposited conductive material thickness, such as between about 1% and about 40% of the deposited conductive material thickness. The processes described herein have been observed herein to produce a protrusion between about 20% and about 30% of the deposited material thickness.

[0154] The amount or size of the protrusion 500 may be controlled, for example, by varying the chemistry used in the process, the power application, such as power levels, and pulse modulation technique. The invention contemplates that the compositions described herein and the power applications described herein may be varied beyond the illustrative examples detailed herein to achieve the formation of a protrusion herein and/or the relative removal rates over wide and narrow feature definitions.

[0155] The size of the protrusions may be controlled by the amount of corrosion inhibitor and/or chelating agents, the pH levels, the power application levels, and process parameters of a pulse modulation technique, or a combination thereof, as described herein. For example, increase amounts of corrosion inhibitor were observed to increase the amount protrusion over wide features as compared to reduced amounts of corrosion inhibitors.

[0156] In one comparison example under identical polishing conditions for a polishing layer of about 11,500 Å thick with a step height of about 6,000 Å, a polishing process with a composition of 0.3 wt.% benzotriazole (BTA) as a corrosion inhibitor exhibited a protrusion height of about 4,200 Å, about a 36.5% protrusion of the deposited conductive material, and a polishing process with a composition of 0.2 wt.% BTA as a corrosion inhibitor exhibited a protrusion height of about 800 Å, about a 7% protrusion of the deposited conductive material. In another comparison example, under identical polishing conditions but different from the first comparison example, a polishing process with a composition of 0.3 wt.% BTA as a corrosion inhibitor exhibited a protrusion of about 2,500 Å, about a 22% protrusion of the deposited conductive material, and a polishing process with a composition of 0.2

wt.% BTA as a corrosion inhibitor exhibited a protrusion of about 0 Å, or no observable protrusion.

[0157] The pH of the composition has also been observed to affect the amount of protrusion. Compositions having less acidic composition were also observed to have greater protrusion height over composition with more acidic compositions. In a comparison example under identical polishing conditions, a polishing process with a pH of 6.5 exhibited a protrusion height of about 3,000 Å, about a 26% protrusion of the deposited conductive material, a polishing process with a pH of about 5.8 exhibited a protrusion height of about 200 Å, about a 1.7% protrusion of the deposited conductive material, and a polishing process with a pH of about 4.5 exhibited a protrusion height of about 0 Å, or no observable protrusion height. Further, a balance of pH and corrosion inhibitor concentration may be used to provide for a selective amount of protrusion. For example a lower pH at a lower corrosion inhibitor concentration may produce the same amount of protrusion as a higher pH with a greater corrosion inhibitor concentration.

[0158] Power application may also be adapted to control the amount of protrusion in the process. For example, with same or similar processing compositions, a power application with a greater amount of power application in the "on" portion of the pulse modulation technique exhibited greater protrusion height formation than a power application with a lesser amount of applied power in the "on" portion of the pulse modulation technique. Power applied during the process may be referenced as voltage, current, current density, wattage, or other suitable means for monitoring and controlling the anodic dissolution process. A greater amount of power application may be achieved, for example, by an increase in the power level, i.e., increase voltage, current, current density, or wattage, an increase in the duration of a power period or pulse, or a combination thereof. Power and pulse modulation techniques may be varied based on changes in the processing parameters, for example, different electrolyte composition, may have different conductivities, and may require different power levels and pulse modulations.

[0159] It is believed that when power is applied, the "on" position, the formation of the passivation layer may increase in thickness and/or density because of metal

ions complexing with components of the passivation layer, and in the "off "position, the passivation layer is subject to more abrasion and removal, due to ion starvation in the electrolyte near the surface of the conductive material being removed. An increase in thickness or density of the passivation layer is believed to result in better chemical and/or electrical insulative properties as well as increased resistance to removal by abrasion.

[0160] Thus, an increase in the total power applied to the substrate, such as an increase in the duration or magnitude of the applied power has been observed to result in increased protrusion height. In one comparison example using a composition having 0.3 wt% BTA and a pH of about 6.5 under similar processing conditions, a protrusion height of about 4,000 Å for a metal layer of about 11,500 Å or less, about a 35% protrusion of the deposited conductive material, was observed to be formed under an "on" only power application, while a pulse modulation technique of 5 seconds "on" and 5 seconds "off" has been observed to result in a protrusion height of less than 400 Å.

[0161] Referring to Figure 4E, any remaining conductive material and barrier layer material may then be polished by a second polishing step to provide a planarized substrate surface. The remaining conductive material and barrier layer material may be removed by at least a chemical mechanical polishing process. Since chemical mechanical polishing processes have been observed to remove material from over in wide feature definitions at higher removal rates as compared to material disposed over narrow feature definitions, the protrusion 500 of conductive material allows for planarization of the conductive material without dishing in the wide feature definitions and minimal or no residue formation over narrow feature definitions. An example of a copper polishing process is disclosed in United States Patent Application No. 10/025,144, filed on December 18, 2001, and entitled "Method And Apparatus For Polishing Metal And Dielectric Substrates", [Attorney Docket No. 5999], and an example of a barrier polishing process is disclosed in United States Patent Application Serial No. 10/193,810, filed On July 11, 2002, and entitled "Dual Reduced Agents For Barrier Removal In Chemical Mechanical Polishing", [Attorney Docket No. 5845.02], which are both incorporated herein to the extent not inconsistent with the claims aspects and disclosure herein.

[0162] The second polishing step may also be an electrochemical mechanical polishing step as described herein. The second electrochemical mechanical polishing step may be adapted to have material disposed on the substrate surface removed at higher removal rates over wide feature definitions as compared to the first polishing step or as compared to removal rates of material disposed over narrow feature definitions to provide for planarization of the conductive material. The relative removal rates of the second electrochemical mechanical polishing step may be adapted to be comparable to removal rate profiles observed in chemical mechanical polishing processes as described herein.

[0163] The removal rate profile of the second electrochemical mechanical polishing process to match chemical mechanical polishing techniques may be achieved by several approaches. In one example, a first electrochemical mechanical polishing step may have a greater amount of corrosion inhibitor or higher pH than a second electrochemical mechanical polishing step allowing for protrusion formation in the first electrochemical mechanical polishing step and no protrusion development in the second electrochemical mechanical polishing step. In another example, a pulse modulation technique for the second electrochemical mechanical polishing step may be used that increases removal rate over wide features as compared to a pulse modulation technique in the first electrochemical mechanical polishing step to control protrusion formation and relative removal rates. A combination of both pH and pulse modulation techniques may be used for both the first and second electrochemical mechanical polishing processes to provide the desired removal rate profiles to produce or remove protrusions as desired.

[0164] Additionally, when the second polishing step is a chemical mechanical polishing step, a composition for the chemical mechanical polishing process may be adapted to provide a desired profile for planarizing the substrate as described for the second electrochemical mechanical polishing step. For example, the chemical mechanical polishing process may have a lesser amount of corrosion inhibitor or lower pH than the electrochemical mechanical polishing step allowing for protrusion formation in the electrochemical mechanical polishing step and no protrusion development and/or protrusion removal in the chemical mechanical polishing step.

[0165] After conductive material and barrier material removal processing steps, the substrate may then be buffed and clean as described herein with respect to claims 5A-5E.

[0166] It has been observed that substrate planarized by the processes described herein have exhibited reduced topographical defects, such as dishing, reduced residues, improved planarity, and improved substrate finish. The processes described herein may be further disclosed by the examples as follows.

Examples:

[0167] The following non-limiting examples are provided to further illustrate embodiments of the invention. However, the examples are not intended to be all-inclusive and are not intended to limit the scope of the inventions described herein.

Polishing Composition Examples/Baselines

Baseline Example

[0168] In an embodiment of the present invention the substrate 208 is placed in a polishing composition containing an acid based electrolyte system, one or more chelating agents, one or more corrosion inhibitors, one or more pH adjusting agents, one or more additives, and a solvent or combination thereof. The substrate surface is anodically biased relative to the electrode 209 by use of the power supply 200 to a voltage of about 2.9 volts. A pressure of 0.2 psi is applied to the substrate by the polishing head 202, pushing it against the conductive pad 203. The substrate 208 and the conductive pad 203 are moved relative to each other. The combination of the above elements of this embodiment can deliver a material removal rate of about 4000 Angstroms per minute. One will note that the magnitude of the bias voltage applied between the electrode 209 and the substrate 208 to achieve this material removal rate, is dependent on many factors including the electrolyte conductivity and the distance between the electrode 209 and the substrate 208. An example of a possible polishing composition is shown in Example 1 in the Composition Examples shown below.

Oxidizing Agent Example

[0169] In another embodiment an oxidizing agents is added to the polishing composition of the Baseline Example described above, which changes the attachment strength of the complexed metal ion to the surface of the substrate. Due to weaker attachment force of the complexed metal ions, due to the presence of the oxidizing agent, the material removal rate can be increased even if the applied pressure and bias voltage are held constant relative to the Baseline Example (shown above). At a pressure of 0.2 psi a removal rate of about 6000 Angstroms per minute has been achieved. An example of a possible polishing composition for this embodiment is shown in Example 2 in the Composition Examples shown below.

Abrasive Particle Example

[0170] In yet another embodiment abrasive particles are added to the polishing composition of the Baseline Example described above. In this embodiment an improved surface finish and material removal rate can be achieved, even if the applied pressure and bias voltage are held constant, relative to the Baseline Example. The increased material removal rate and improved surface finish is likely due to the increased contact area between the conductive pad 203 and the substrate surface. The increased contact area appears to help to more efficiently remove the complexed metal ions even though they may have a high attachment strength. At a pressure of 0.2 psi and similar bias voltage as the Baseline Example, a removal rate of about 4800 Angstroms per minute can be achieved. The surface finish achieved using this embodiment is comparable (same order of magnitude) to a surface finish found by use of a conventional CMP process. An example of a possible polishing composition for this embodiment is shown in Example 3 in the Composition Examples shown below.

Oxidizing Agent and Abrasive Particle Example

[0171] In yet another embodiment, abrasive particles and one or more oxidizing agents are added to the polishing composition of the Baseline Example to increase the removal rate and produce a better surface finish. This can be achieved even though the applied pressure and bias voltage are held constant, relative to the Baseline Example shown above. A pressure of 0.2 psi and similar bias voltage can achieve a removal rate of about 6000 Angstroms per minute while achieving a

surface finish comparable to a conventional CMP process. An example of a possible polishing composition for this embodiment is shown in Example 4 in the Composition Examples shown below.

[0172] Therefore, one feature of the present invention is that it makes it possible to adjust the pad pressure and polishing composition components to enhance the material removal rate, while minimizing the formation of topographical defects.

Composition Examples:

[0173] The following non-limiting examples are provided to further illustrate embodiments of the invention. However, the examples are not intended to be all inclusive and are not intended to limit the scope of the invention described herein.

Example 1:

[0174] A copper plated substrate was polished and planarized using the following polishing composition within a modified cell on a Reflection® system, available from Applied Materials, Inc. of Santa Clara, California.

about 6% by volume phosphoric acid;
about 2% by volume ethylenediamine;
about 2% by weight ammonium citrate;
about 0.3% by weight benzotriazole;
between about 2% and about 6% by volume of potassium hydroxide to provide a pH of about 5; and
deionized water.

Example 2:

[0175] A copper plated substrate was polished and planarized using the following polishing composition within a modified cell on a Reflection® system, available from Applied Materials, Inc. of Santa Clara, California.

about 6% by volume phosphoric acid;
about 2% by volume ethylenediamine;

about 2% by weight ammonium citrate;

about 0.3% by weight benzotriazole;

between about 2% and about 6% by volume of potassium hydroxide to provide a pH of about 5;

about 0.45% by volume of hydrogen peroxide; and

deionized water.

Example 3:

[0176] A copper plated substrate was polished and planarized using the following polishing composition within a modified cell on a Reflection® system, available from Applied Materials, Inc. of Santa Clara, California.

about 6% by volume phosphoric acid;

about 2% by volume ethylenediamine;

about 2% by weight ammonium citrate;

about 0.3% by weight benzotriazole;

between about 2% and about 6% by volume of potassium hydroxide to provide a pH of about 6;

about 0.1% by weight of silica (SiO_2) abrasive particles; and

deionized water.

Example 4:

[0177] A copper plated substrate was polished and planarized using the following polishing composition within a modified cell on a Reflection® system, available from Applied Materials, Inc. of Santa Clara, California.

about 6% by volume phosphoric acid;

about 2% by volume ethylenediamine;

about 2% by weight ammonium citrate;

about 0.3% by weight benzotriazole;

between about 2% and about 6% by volume of potassium hydroxide to provide a pH of about 5;

about 0.45% by volume of hydrogen peroxide;

about 0.15% by weight of silica ($SiO2$) abrasive particles; and

deionized water.

Example 5:

[0178] A copper plated substrate was polished and planarized using the following polishing composition within a modified cell on a Reflection® system, available from Applied Materials, Inc. of Santa Clara, California.

about 1.5% by volume phosphoric acid;

about 0.4% by volume ethylenediamine;

about 0.8% by weight ammonium citrate;

about 0.25% by weight benzotriazole;

between about 0.5% and about 3% by volume of 40 % potassium hydroxide solution to provide a pH of about 5.4;

about 0.5% by volume of hydrogen peroxide; and

deionized water.

Example 6:

[0179] A copper plated substrate was polished and planarized using the following polishing composition within a modified cell on a Reflection® system, available from Applied Materials, Inc. of Santa Clara, California.

about 1.5% by volume phosphoric acid;

about 0.4% by volume ethylenediamine;

about 0.8% by weight ammonium citrate;

about 0.25% by weight benzotriazole;

between about 0.5% and about 3% by volume of 40 % potassium hydroxide solution to provide a pH of about 5.4;

about 0.7% by weight of silica ($SiO2$) abrasive particles; and

deionized water.

Example 7:

[0180] A copper plated substrate was polished and planarized using the following polishing composition within a modified cell on a Reflection® system, available from Applied Materials, Inc. of Santa Clara, California.

about 1.5% by volume phosphoric acid;
about 0.4% by volume ethylenediamine;
about 0.8% by weight ammonium citrate;
about 0.25% by weight benzotriazole;
between about 0.5% and about 3% by volume of 40 % potassium hydroxide solution to provide a pH of about 5.4;
about 0.5% by volume of hydrogen peroxide;
about 0.7% by weight of silica ($SiO2$) abrasive particles; and
deionized water.

Example 8:

[0181] A copper plated substrate was polished and planarized using the following polishing composition within a modified cell on a Reflection® system, available from Applied Materials, Inc. of Santa Clara, California.

about 1.5% by volume phosphoric acid;
about 0.4% by volume ethylenediamine;
about 0.8% by weight ammonium citrate;
about 0.25% by weight benzotriazole;
about 0.2% by weight polyethylene glycol;
from about 0.5% to about 3% by volume 40% KOH solution to provide a pH of about 5.4;
about 0.5% by volume of hydrogen peroxide;
about 0.7% by weight of silica ($SiO2$) abrasive particles; and
de-ionized water.

Example 9:

[0182] A copper plated substrate was polished and planarized using the following polishing composition within a modified cell on a Reflection® system, available from Applied Materials, Inc. of Santa Clara, California.

about 1.0% by volume phosphoric acid;
about 0.5% by volume glycine;
about 0.35% by weight benzotriazole;
from about 0.5% to about 3% by volume 40% KOH solution to provide a pH of about 4.9;
about 0.5% by volume of hydrogen peroxide;
about 0.7% by weight of silica ($SiO2$) abrasive particles; and
de-ionized water.

Example 10:

[0183] A copper plated substrate was polished and planarized using the following polishing composition within a modified cell on a Reflection® system, available from Applied Materials, Inc. of Santa Clara, California.

about 0.6% by volume phosphoric acid;
about 1.0% by volume glycine;
about 0.35% by weight benzotriazole;
from about 0.5% to about 3% by volume 40% KOH solution to provide a pH of about 6.1;
about 0.5% by volume of hydrogen peroxide;
about 0.7% by weight of silica ($SiO2$) abrasive particles; and
de-ionized water.

Two-Step Polishing Examples:

Example 1:

[0184] A copper plated substrate with 300 mm diameter was polished and planarized using the following polishing composition within a modified cell on a

REFLEXION® system, available from Applied Materials, Inc. of Santa Clara, California. A substrate having a copper layer of about 11,500 Å thick on the substrate surface with a step height of about 6,000 Å was placed onto the first platen and exposed to a polishing composition of:

about 6% by volume phosphoric acid;
about 2% by volume ethylenediamine;
about 2% by weight ammonium citrate;
about 0.3% by weight benzotriazole;
from about 2% to about 6% by volume 40% KOH solution to provide a pH of about 5;
about 0.45% by volume of hydrogen peroxide;
about 0.15% by weight of silica (SiO2) abrasive particles; and
de-ionized water.

[0185] A polishing article was contacted with the substrate at about 0.2 psi and a bias of about 25 mA/cm2 (about 17-18 amps or about 3 volts) was applied during the process. The substrate was polished and examined. The copper layer thickness was reduced to about 1,500 Å.

[0186] The substrate was placed onto the second platen and exposed subsequently exposed to a polishing composition of:

about 1.5% by volume phosphoric acid;
about 0.4% by volume ethylenediamine;
about 0.8% by weight ammonium citrate;
about 0.25% by weight benzotriazole;
from about 0.5% to about 3% by volume 40% KOH solution to provide a pH of about 5.4;
about 0.5% by volume of hydrogen peroxide;
about 0.7% by weight of silica (SiO2) abrasive particles; and
de-ionized water.

[0187] A polishing article was contacted with the substrate at about 0.1 psi at a bias of about 7 mA/cm2 (about 4-5 amps or about 1.5 volts) was applied during the process. The substrate was polished and examined. The excess copper layer

formerly on the substrate surface was removed to leave behind the barrier layer and the copper trench.

Example 2:

[0188] A copper plated substrate with 300 mm diameter was polished and planarized using the following polishing composition within a modified cell on a REFLEXION® system, available from Applied Materials, Inc. of Santa Clara, California. A substrate having a copper layer of about 11,500 Å thick on the substrate surface with a step height of about 6,000 Å was placed into the first platen and exposed to a polishing composition of:

about 6% by volume phosphoric acid;
about 2% by volume ethylenediamine;
about 2% by weight ammonium citrate;
about 0.3% by weight benzotriazole;
from about 2% to about 6% by volume 40% KOH solution to provide a pH of about 5;
about 0.45% by volume of hydrogen peroxide;
about 0.15% by weight of silica (SiO2) abrasive particles; and
de-ionized water.

[0189] A polishing article was contacted with the substrate at about 0.2 psi and a bias of about 25 mA/cm2 (about 17-18 amps or about 3 volts) was applied during the process. The substrate was polished and examined. The copper layer thickness was reduced to about 1,500 Å.

[0190] The substrate was placed into the second platen and exposed subsequently exposed to a polishing composition of:

about 1.5% by volume phosphoric acid;
about 0.4% by volume ethylenediamine;
about 0.8% by weight ammonium citrate;
about 0.25% by weight benzotriazole;
about 0.2% by weight polyethylene glycol;

from about 0.5% to about 3% by volume 40% KOH solution to provide a pH of about 5.4;

about 0.5% by volume of hydrogen peroxide;

about 0.7% by weight of silica (SiO2) abrasive particles; and

de-ionized water.

[0191] A polishing article was contacted with the substrate at about 0.1 psi at a bias of about 7 mA/cm^2 (about 4-5 amps or about 1.5 volts) was applied during the process. The substrate was polished and examined. The excess copper layer formerly on the substrate surface was removed to leave behind the barrier layer and the copper trench.

Example 3:

[0192] A copper plated substrate with 300 mm diameter was polished and planarized using the following polishing composition within a modified cell on a REFLEXION® system, available from Applied Materials, Inc. of Santa Clara, California. A substrate having a copper layer of about 11,500 Å thick on the substrate surface with a step height of about 6,000 Å was placed into the first platen and exposed to a polishing composition of:

about 6% by volume phosphoric acid;

about 2% by volume ethylenediamine;

about 2% by weight ammonium citrate;

about 0.3% by weight benzotriazole;

from about 2% to about 6% by volume 40% KOH solution to provide a pH of about 5;

about 0.45% by volume of hydrogen peroxide;

about 0.15% by weight of silica (SiO_2) abrasive particles; and

de-ionized water.

[0193] A polishing article was contacted with the substrate at about 0.2 psi and a bias of about 25 mA/cm^2 (about 17-18 amps or about 3 volts) was applied during the process. The substrate was polished and examined. The copper layer thickness was reduced to about 1,500 Å.

[0194] The substrate was placed into the second platen and exposed subsequently exposed to a polishing composition of:

about 1.0% by volume phosphoric acid;
about 0.5% by volume glycine;
about 0.35% by weight benzotriazole;
from about 0.5% to about 3% by volume 40% KOH solution to provide a pH of about 4.9;
about 0.5% by volume of hydrogen peroxide;
about 0.7% by weight of silica (SiO_2) abrasive particles; and
de-ionized water.

[0195] A polishing article was contacted with the substrate at about 0.1 psi at a bias of about 7 mA/cm^2 (about 4-5 amps or about 1.5 volts) was applied during the process. The substrate was polished and examined. The excess copper layer formerly on the substrate surface was removed to leave behind the barrier layer and the copper trench.

Example 4:

[0196] A copper plated substrate with 300 mm diameter was polished and planarized using the following polishing composition within a modified cell on a REFLEXION® system, available from Applied Materials, Inc. of Santa Clara, California. A substrate having a copper layer of about 11,500 Å thick on the substrate surface with a step height of about 6,000 Å was placed into the first platen and exposed to a polishing composition of:

about 6% by volume phosphoric acid;
about 2% by volume ethylenediamine;
about 2% by weight ammonium citrate;
about 0.3% by weight benzotriazole;
from about 2% to about 6% by volume 40% KOH solution to provide a pH of about 5;
about 0.45% by volume of hydrogen peroxide;
about 0.15% by weight of silica (SiO_2) abrasive particles; and
de-ionized water.

[0197] A polishing article was contacted with the substrate at about 0.2 psi and a bias of about 25 mA/cm^2 (about 17-18 amps or about 3 volts) was applied during the process. The substrate was polished and examined. The copper layer thickness was reduced to about 1,500 Å.

[0198] The substrate was placed into the second platen and exposed subsequently exposed to a polishing composition of:

about 0.6% by volume phosphoric acid;
about 1.0% by volume glycine;
about 0.35% by weight benzotriazole;
from about 0.5% to about 3% by volume 40% KOH solution to provide a pH of about 6.1;
about 0.5% by volume of hydrogen peroxide;
about 0.7% by weight of silica (SiO_2) abrasive particles; and
de-ionized water.

[0199] A polishing article was contacted with the substrate at about 0.1 psi at a bias of about 7 mA/cm^2 (about 4-5 amps or about 1.5 volts) was applied during the process. The substrate was polished and examined. The excess copper layer formerly on the substrate surface was removed to leave behind the barrier layer and the copper trench.

Example 5:

[0200] A copper plated substrate with 300 mm diameter was polished and planarized using the following polishing composition within a modified cell on a REFLEXION® system, available from Applied Materials, Inc. of Santa Clara, California. A substrate having a copper layer of about 11,500 Å thick on the substrate surface with a step height of about 6,000 Å was placed into the first platen and exposed to a polishing composition of:

about 6% by volume phosphoric acid;
about 2% by volume ethylenediamine;
about 2% by weight ammonium citrate;
about 0.3% by weight benzotriazole;

from about 2% to about 6% by volume 40% KOH solution to provide a pH of about 5;

about 0.45% by volume of hydrogen peroxide;

about 0.15% by weight of silica (SiO_2) abrasive particles; and

de-ionized water.

[0201] A polishing article was contacted with the substrate at about 0.2 psi and a bias of about 25 mA/cm^2 (about 17-18 amps or about 3 volts) was applied during the process. The substrate was polished and examined. The copper layer thickness was reduced to about 1,500 Å.

[0202] The substrate was placed into the second platen and exposed subsequently exposed to a polishing composition of:

about 0.6% by volume phosphoric acid;

about 1.5% by volume glycine;

about 0.35% by weight benzotriazole;

from about 0.5% to about 3% by volume 40% KOH solution to provide a pH of about 6.1;

about 0.5% by volume of hydrogen peroxide;

about 0.7% by weight of silica (SiO_2) abrasive particles; and

de-ionized water.

[0203] A polishing article was contacted with the substrate at about 0.1 psi at a bias of about 7 mA/cm^2 (about 4-5 amps or about 1.5 volts) was applied during the process. The substrate was polished and examined. The excess copper layer formerly on the substrate surface was removed to leave behind the barrier layer and the copper trench.

Example 6:

[0204] A copper plated substrate with 300 mm diameter was polished and planarized using the following polishing composition within a modified cell on a REFLEXION® system, available from Applied Materials, Inc. of Santa Clara, California. A substrate having a copper layer of about 11,500 Å thick on the substrate surface with a step height of about 6,000 Å was placed into the first platen and exposed to a polishing composition of:

about 6% by volume phosphoric acid;

about 2% by volume ethylenediamine;

about 2% by weight ammonium citrate;

about 0.3% by weight benzotriazole;

from about 2% to about 6% by volume 40% KOH solution to provide a pH of about 5;

about 0.45% by volume of hydrogen peroxide;

about 0.15% by weight of silica (SiO_2) abrasive particles; and

de-ionized water.

[0205] A polishing article was contacted with the substrate at about 0.2 psi and a bias of about 25 mA/cm^2 (about 17-18 amps or about 3 volts) was applied during the process. The substrate was polished and examined. The copper layer thickness was reduced to about 1,500 Å.

[0206] The substrate was placed into the second platen and exposed subsequently exposed to a polishing composition of:

about 0.6% by volume phosphoric acid;

about 2.0% by volume glycine;

about 0.35% by weight benzotriazole;

from about 0.5% to about 3% by volume 40% KOH solution to provide a pH of about 6.1;

about 0.5% by volume of hydrogen peroxide;

about 0.7% by weight of silica (SiO_2) abrasive particles; and

de-ionized water.

[0207] A polishing article was contacted with the substrate at about 0.1 psi at a bias of about 7 mA/cm^2 (about 4-5 amps or about 1.5 volts) was applied during the process. The substrate was polished and examined. The excess copper layer formerly on the substrate surface was removed to leave behind the barrier layer and the copper trench.

Example 7:

[0208] A copper plated substrate with 300 mm diameter was polished and planarized using the following polishing composition within a modified cell on a

REFLEXION® system, available from Applied Materials, Inc. of Santa Clara, California. A substrate having a copper layer of about 11,500 Å thick on the substrate surface with a step height of about 6,000 Å was placed into the first platen and exposed to a polishing composition of:

about 6% by volume phosphoric acid;
about 2% by volume ethylenediamine;
about 2% by weight ammonium citrate;
about 0.3% by weight benzotriazole;
from about 2% to about 6% by volume 40% KOH solution to provide a pH of about 5;
about 0.45% by volume of hydrogen peroxide;
about 0.15% by weight of silica (SiO_2) abrasive particles; and
de-ionized water.

[0209] A polishing article was contacted with the substrate at about 0.2 psi and a bias of about 25 mA/cm^2 (about 17-18 amps or about 3 volts) was applied during the process. The substrate was polished and examined. The copper layer thickness was reduced to about 1,500 Å.

[0210] The substrate was placed into the second platen and exposed subsequently exposed to a polishing composition of:

about 1.5% by volume phosphoric acid;
about 0.4% by volume ethylenediamine;
about 0.8% by weight ammonium citrate;
about 0.25% by weight benzotriazole;
from about 0.5% to about 3% by volume 40% KOH solution to provide a pH of about 5.4;
about 0.7% by weight of silica (SiO_2) abrasive particles; and
de-ionized water.

[0211] A polishing article was contacted with the substrate at about 0.1 psi at a bias of about 7 mA/cm^2 (about 4-5 amps or about 1.5 volts) was applied during the process. The substrate was polished and examined. The excess copper layer

formerly on the substrate surface was removed to leave behind the barrier layer and the copper trench.

Example 8:

[0212] A copper plated substrate with 300 mm diameter was polished and planarized using the following polishing composition within a modified cell on a REFLEXION® system, available from Applied Materials, Inc. of Santa Clara, California. A substrate having a copper layer of about 11,500 Å thick on the substrate surface with a step height of about 6,000 Å was placed into the first platen and exposed to a polishing composition of:

about 6% by volume phosphoric acid;
about 2% by volume ethylenediamine;
about 2% by weight ammonium citrate;
about 0.3% by weight benzotriazole;
from about 2% to about 6% by volume 40% KOH solution to provide a pH of about 5;
about 0.45% by volume of hydrogen peroxide;
about 0.15% by weight of silica (SiO_2) abrasive particles; and
de-ionized water.

[0213] A polishing article was contacted with the substrate at about 0.2 psi and a bias of about 25 mA/cm^2 (about 17-18 amps or about 3 volts) was applied during the process. The substrate was polished and examined. The copper layer thickness was reduced to about 1,500 Å.

[0214] The substrate was placed into the second platen and exposed subsequently exposed to a polishing composition of:

about 1.5% by volume phosphoric acid;
about 0.4% by volume ethylenediamine;
about 0.8% by weight ammonium citrate;
about 0.25% by weight benzotriazole;
about 0.2% by weight polyethylene glycol;
from about 0.5% to about 3% by volume 40% KOH solution to provide a pH of about 5.4;

about 0.7% by weight of silica (SiO_2) abrasive particles; and

de-ionized water.

[0215] A polishing article was contacted with the substrate at about 0.1 psi at a bias of about 7 mA/cm^2 (about 4-5 amps or about 1.5 volts) was applied during the process. The substrate was polished and examined. The excess copper layer formerly on the substrate surface was removed to leave behind the barrier layer and the copper trench.

Example 9:

[0216] A copper plated substrate with 300 mm diameter was polished and planarized using the following polishing composition within a modified cell on a REFLEXION® system, available from Applied Materials, Inc. of Santa Clara, California. A substrate having a copper layer of about 11,500 Å thick on the substrate surface with a step height of about 6,000 Å was placed into the first platen and exposed to a polishing composition of:

about 6% by volume phosphoric acid;

about 2% by volume ethylenediamine;

about 2% by weight ammonium citrate;

about 0.3% by weight benzotriazole;

from about 2% to about 6% by volume 40% KOH solution to provide a pH of about 5;

about 0.45% by volume of hydrogen peroxide;

about 0.15% by weight of silica (SiO_2) abrasive particles; and

de-ionized water.

[0217] A polishing article was contacted with the substrate at about 0.2 psi and a bias of about 25 mA/cm^2 (about 17-18 amps or about 3 volts) was applied during the process. The substrate was polished and examined. The copper layer thickness was reduced to about 1,500 Å.

[0218] The substrate was placed into the second platen and exposed subsequently exposed to a polishing composition of:

about 1.0% by volume phosphoric acid;

about 0.5% by volume glycine;

about 0.35% by weight benzotriazole;

from about 0.5% to about 3% by volume 40% KOH solution to provide a pH of about 4.9;

about 0.7% by weight of silica (SiO_2) abrasive particles; and

de-ionized water.

[0219] A polishing article was contacted with the substrate at about 0.1 psi at a bias of about 7 mA/cm^2 (about 4-5 amps or about 1.5 volts) was applied during the process. The substrate was polished and examined. The excess copper layer formerly on the substrate surface was removed to leave behind the barrier layer and the copper trench.

Example 10:

[0220] A copper plated substrate with 300 mm diameter was polished and planarized using the following polishing composition within a modified cell on a REFLEXION® system, available from Applied Materials, Inc. of Santa Clara, California. A substrate having a copper layer of about 11,500 Å thick on the substrate surface with a step height of about 6,000 Å was placed into the first platen and exposed to a polishing composition of:

about 6% by volume phosphoric acid;

about 2% by volume ethylenediamine;

about 2% by weight ammonium citrate;

about 0.3% by weight benzotriazole;

from about 2% to about 6% by volume 40% KOH solution to provide a pH of about 5;

about 0.45% by volume of hydrogen peroxide;

about 0.15% by weight of silica (SiO_2) abrasive particles; and

de-ionized water.

[0221] A polishing article was contacted with the substrate at about 0.2 psi and a bias of about 25 mA/cm^2 (about 17-18 amps or about 3 volts) was applied during the process. The substrate was polished and examined. The copper layer thickness was reduced to about 1,500 Å.

[0222] The substrate was placed into the second platen and exposed subsequently exposed to a polishing composition of:

about 0.6% by volume phosphoric acid;

about 1.0% by volume glycine;

about 0.35% by weight benzotriazole;

from about 0.5% to about 3% by volume 40% KOH solution to provide a pH of about 6.1;

about 0.7% by weight of silica (SiO_2) abrasive particles; and

de-ionized water.

[0223] A polishing article was contacted with the substrate at about 0.1 psi at a bias of about 7 mA/cm^2 (about 4-5 amps or about 1.5 volts) was applied during the process. The substrate was polished and examined. The excess copper layer formerly on the substrate surface was removed to leave behind the barrier layer and the copper trench.

Example 11:

[0224] A copper plated substrate with 300 mm diameter was polished and planarized using the following polishing composition within a modified cell on a REFLEXION® system, available from Applied Materials, Inc. of Santa Clara, California. A substrate having a copper layer of about 11,500 Å thick on the substrate surface with a step height of about 6,000 Å was placed into the first platen and exposed to a polishing composition of:

about 6% by volume phosphoric acid;

about 2% by volume ethylenediamine;

about 2% by weight ammonium citrate;

about 0.3% by weight benzotriazole;

from about 2% to about 6% by volume 40% KOH solution to provide a pH of about 5;

about 0.45% by volume of hydrogen peroxide;

about 0.15% by weight of silica (SiO_2) abrasive particles; and

de-ionized water.

[0225] A polishing article was contacted with the substrate at about 0.2 psi and a bias of about 25 mA/cm^2 (about 17-18 amps or about 3 volts) was applied during the process. The substrate was polished and examined. The copper layer thickness was reduced to about 1,500 Å.

[0226] The substrate was placed into the second platen and exposed subsequently exposed to a polishing composition of:

about 0.6% by volume phosphoric acid;
about 1.5% by volume glycine;
about 0.35% by weight benzotriazole;
from about 0.5% to about 3% by volume 40% KOH solution to provide a pH of about 6.1;
about 0.7% by weight of silica (SiO_2) abrasive particles; and
de-ionized water.

[0227] A polishing article was contacted with the substrate at about 0.1 psi at a bias of about 7 mA/cm^2 (about 4-5 amps or about 1.5 volts) was applied during the process. The substrate was polished and examined. The excess copper layer formerly on the substrate surface was removed to leave behind the barrier layer and the copper trench.

Example 12:

[0228] A copper plated substrate with 300 mm diameter was polished and planarized using the following polishing composition within a modified cell on a REFLEXION® system, available from Applied Materials, Inc. of Santa Clara, California. A substrate having a copper layer of about 11,500 Å thick on the substrate surface with a step height of about 6,000 Å was placed into the first platen and exposed to a polishing composition of:

about 6% by volume phosphoric acid;
about 2% by volume ethylenediamine;
about 2% by weight ammonium citrate;
about 0.3% by weight benzotriazole;

from about 2% to about 6% by volume 40% KOH solution to provide a pH of about 5;

about 0.45% by volume of hydrogen peroxide;

about 0.15% by weight of silica (SiO_2) abrasive particles; and

de-ionized water.

[0229] A polishing article was contacted with the substrate at about 0.2 psi and a bias of about 25 mA/cm^2 (about 17-18 amps or about 3 volts) was applied during the process. The substrate was polished and examined. The copper layer thickness was reduced to about 1,500 Å.

[0230] The substrate was placed into the second platen and exposed subsequently exposed to a polishing composition of:

about 0.6% by volume phosphoric acid;

about 2.0% by volume glycine;

about 0.35% by weight benzotriazole;

from about 0.5% to about 3% by volume 40% KOH solution to provide a pH of about 6.1;

about 0.7% by weight of silica (SiO_2) abrasive particles; and

de-ionized water.

[0231] A polishing article was contacted with the substrate at about 0.1 psi at a bias of about 7 mA/cm^2 (about 4-5 amps or about 1.5 volts) was applied during the process. The substrate was polished and examined. The excess copper layer formerly on the substrate surface was removed to leave behind the barrier layer and the copper trench.

Protrusion examples:

Example 1:

[0232] A copper plated substrate was polished and planarized using the following polishing composition within a modified cell on a REFLEXION® system, available from Applied Materials, Inc. of Santa Clara, California. A substrate having a copper layer of about 11,500 Å thick on the substrate surface with a step height of about 6,000 Å was exposed to a polishing composition of:

about 6% by volume phosphoric acid;

about 2% by volume ethylenediamine;

about 2% by weight ammonium citrate;

about 0.3% by weight benzotriazole;

between about 2% and about 6% by volume of potassium hydroxide to provide a pH of about 5; and

deionized water, and

a polishing article was contacted with the substrate at about 0.2 psi at a bias of about 3 watts/volts was applied during the process. The substrate was polishing and examined. A protrusion height of about 4,000 Å was observed over wide feature definitions.

Example 2:

[0233] A copper plated substrate was polished and planarized using the following polishing composition within a modified cell on a REFLEXION® system, available from Applied Materials, Inc. of Santa Clara, California. A substrate having a copper layer of about 11,500 Å thick on the substrate surface with a step height of about 6,000 Å was exposed to a polishing composition of:

about 6% by volume phosphoric acid;

about 2% by volume ethylenediamine;

about 2% by weight ammonium citrate;

about 0.3% by weight benzotriazole;

between about 2% and about 6% by volume of potassium hydroxide to provide a pH of about 5; and

deionized water, and

a polishing article was contacted with the substrate at about 0.2 psi at a bias of about 3 watts/volts was applied by a pulse technique of 10 seconds on and 2 seconds off for 8 of cycles. The substrate was polishing and examined. A protrusion height of about 1,500 Å was observed over wide feature definitions.

[0234] 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.

Claims:

1. A method of processing a substrate having a conductive material layer disposed thereon, comprising:

positioning the substrate in a process apparatus;

exposing the substrate to a first polishing composition;

applying a first bias to the substrate;

removing a bulk portion of the conductive material layer;

exposing the substrate to a second polishing composition; and then

polishing the substrate to remove a residual portion of the conductive material layer.

2. The method of claim 1, wherein the removing the bulk portion of the conductive layer comprises removing at least 50% of the conductive material layer.

3. The method of claim 2, wherein the removing the bulk portion of the conductive layer comprises removing at least 80% of the conductive material layer.

4. The method of claim 1, wherein the conductive material layer comprises copper or a copper alloy.

5. The method of claim 1, wherein the first polishing composition comprises:

phosphoric acid;

at least one chelating agent;

a corrosion inhibitor;

a salt;

an oxidizer; and

abrasive particulates.

6. The method of claim 5, wherein the first polishing composition comprises:

from about 1 wt% to about 10 wt% of phosphoric acid;

from about 0.1 wt% to about 6 wt% of the at least one chelating agent;

from about 0.01 wt% to about 1 wt% of the corrosion inhibitor;

from about 0.5 wt% to about 10 wt% of the salt;
from about 0.2 wt% to about 5 wt% of the oxidizer; and
from about 0.05 wt% to about 1 wt% of the abrasive particulates.

7 The method of claim 1, wherein the second polishing composition comprises:
phosphoric acid;
at least one chelating agent; and
a corrosion inhibitor.

8 The method of claim 7, wherein the second polishing composition comprises:
from about 0.1 wt% to about 5 wt% of phosphoric acid;
from about 0.1 wt% to about 5 wt% of at least one chelating agent; and
from about 0.01 wt% to about 1 wt% of the corrosion inhibitor.

9. The method of claim 7, wherein
the at least one chelating agent of the second polishing composition is selected from the group consisting of glycine, ethylenediamine, ethylenediamine tetraacetate, citric acid, ammonium citrate, salts thereof, derivatives thereof, and combinations thereof,
the corrosion inhibitor of the second polishing composition is selected from the group consisting of benzotriazole, 5-methyl-1-benzotriazole, salts thereof, derivatives thereof, and combinations thereof.

10. The method of claim 7, wherein
the corrosion inhibitor of the second polishing composition is benzotriazole; and
the at least one chelating agent of the second polishing composition is glycine or ethylenediamine and ammonium citrate.

11. The method of claim 10, wherein the second polishing composition further comprises polyethylene glycol.

12. The method of claim 7, wherein the second polishing composition further comprises at least one member selected from the group consisting of:

abrasive particulates,

hydrogen peroxide and derivatives thereof,

at least one pH adjusting agent to provide a pH from about 4 to about 7;

a solvent; and combinations thereof.

13. The method of claim 1, wherein the first polishing composition has a conductivity in a range from about 30 mS to about 60 mS.

14. The method of claim 13, wherein the second polishing composition has a conductivity in a range from about 15 mS to about 40 mS.

15. The method of claim 1, wherein the first bias is applied to a substrate at a current density between about 0.01 milliamps/cm^2 and about 100 milliamps/cm^2.

16. The method of claim 1, further comprising:

contacting the substrate with a polishing article at a contact pressure between about 0.01 psi and about 1 psi between the substrate and a polishing article; and

providing relative motion between the substrate and the polishing article.

17. The method of claim 1, wherein the polishing the substrate to remove a residual portion of the conductive material comprising polishing the substrate by a chemical mechanical polishing process.

18. The method of claim 1, wherein the polishing the substrate by at least a chemical mechanical polishing process comprises:

exposing the substrate to a second polishing composition;

applying a second// bias to the substrate;

contacting the substrate with a polishing article at a contact pressure between about 0.01 psi and about 1 psi between the substrate and a polishing article; and

providing relative motion between the substrate and the polishing article.

19. The method of claim 1, wherein removing a bulk portion of the conductive material layer is performed on a first removing a residual portion of the conductive material layer is performed on a second platen.

20. A method of processing a substrate having a conductive material layer disposed thereon, comprising:

positioning the substrate in a process apparatus comprising a first electrode and a second electrode;

supplying a first polishing composition between the first electrode and the substrate, wherein the first polishing composition comprises:

phosphoric acid;

at least one chelating agent;

a corrosion inhibitor;

a salt;

an oxidizer;

abrasive particulates;

at least one pH adjusting agent to provide a pH from about 4 to about 7; and

a solvent;

forming a passivation layer on the conductive material layer;

removing the passivation layer to expose a portion of the conductive material layer;

applying a first bias between the first electrode and the second electrode;

removing a first portion of the conductive material layer;

separating the substrate from the first polishing composition;

exposing the substrate to a second polishing composition, wherein the second polishing composition comprises:

phosphoric acid;

at least one chelating agent; and

a corrosion inhibitor; and then

polishing the substrate to remove a second portion of the conductive material layer.

21. The method of claim 20, wherein the removing the bulk portion of the conductive layer comprises removing at least 50% of the conductive material layer.

22. The method of claim 21, wherein the removing the bulk portion of the conductive layer comprises removing at least 80% of the conductive material layer.

23. The method of claim 20, wherein the conductive material layer comprises copper or a copper alloy.

24. The method of claim 20, wherein the first polishing composition comprises:

from about 1 wt% to about 10 wt% of phosphoric acid;
from about 0.1 wt% to about 6 wt% of the at least one chelating agent;
from about 0.01 wt% to about 1 wt% of the corrosion inhibitor;
from about 0.5 wt% to about 10 wt% of the salt;
from about 0.2 wt% to about 5 wt% of the oxidizer; and
from about 0.05 wt% to about 1 wt% of the abrasive particulates.

25 The method of claim 20, wherein the second polishing composition comprises:

from about 0.1 wt% to about 5 wt% of phosphoric acid;
from about 0.1 wt% to about 5 wt% of at least one chelating agent; and
from about 0.01 wt% to about 1 wt% of the corrosion inhibitor.

26. The method of claim 20, wherein

the at least one chelating agent of the second polishing composition is selected from the group consisting of glycine, ethylenediamine, ethylenediamine tetraacetate, citric acid, ammonium citrate, salts thereof, derivatives thereof, and combinations thereof,

the corrosion inhibitor of the second polishing composition is selected from the group consisting of benzotriazole, 5-methyl-1-benzotriazole, salts thereof, derivatives thereof, and combinations thereof.

27. The method of claim 20, wherein

the corrosion inhibitor of the second polishing composition is benzotriazole; and

the at least one chelating agent of the second polishing composition is glycine or ethylenediamine and ammonium citrate.

28. The method of claim 27, wherein the second polishing composition further comprises polyethylene glycol.

29. The method of claim 20, wherein the second polishing composition further comprises at least one member selected from the group consisting of:

abrasive particulates,

hydrogen peroxide and derivatives thereof,

at least one pH adjusting agent to provide a pH from about 4 to about 7;

a solvent; and combinations thereof.

30. The method of claim 20, wherein the first polishing composition has a conductivity in a range from about 30 mS to about 60 mS.

31. The method of claim 30, wherein the second polishing composition has a conductivity in a range from about 15 mS to about 40 mS.

32. The method of claim 20, wherein the first bias is applied to a substrate at a current density between about 0.01 milliamps/cm^2 and about 100 milliamps/cm^2.

33. The method of claim 20, further comprising:

contacting the substrate with a polishing article at a contact pressure between about 0.01 psi and about 1 psi between the substrate and a polishing article; and

providing relative motion between the substrate and the polishing article.

34. The method of claim 20, wherein the polishing the substrate to remove a residual portion of the conductive material comprising polishing the substrate by a chemical mechanical polishing process.

35. The method of claim 20, wherein the polishing the substrate by at least a chemical mechanical polishing process comprises:

exposing the substrate to a second polishing composition;

applying a second bias to the substrate;

contacting the substrate with a polishing article at a contact pressure between about 0.01 psi and about 1 psi between the substrate and a polishing article; and

providing relative motion between the substrate and the polishing article.

36. The method of claim 20, wherein removing a bulk portion of the conductive material layer is performed on a first removing a residual portion of the conductive material layer is performed on a second platen.

37. A method of processing a substrate having a conductive material layer disposed thereon, comprising:

positioning the substrate in a process apparatus;

exposing the substrate to a first polishing composition with a first conductivity in a range from about 30 mS to about 60 mS and comprising an oxidizer and abrasive particulates;

applying a first bias to the substrate;

exposing the substrate to a second polishing composition with a second conductivity in a range from about 15 mS to about 40 mS;

applying a second bias to the substrate; and

continuing to remove the conductive layer.

38. A method of processing a substrate having a conductive material layer disposed thereon, comprising:

positioning the substrate in a process apparatus;

exposing the substrate to a first polishing composition comprising phosphoric acid, at least one chelating agent, a corrosion inhibitor, a salt, an oxidizer, abrasive particulates, at least one pH adjusting agent to provide a pH from about 4 to about 7, and a solvent;

applying a first bias to the substrate;

exposing the substrate to a second polishing composition comprising phosphoric acid, at least one chelating agent, a corrosion inhibitor, abrasive particulates, at least one pH adjusting agent to provide a pH from about 4 to about 7, and a solvent;

applying a second bias to the substrate; and

continuing to remove the conductive layer.

39. A composition for removing at least a conductive material from a substrate surface, comprising:

between about 0.1 wt% and about 5 wt% of a phosphoric acid based electrolyte system;

between about 0.1 wt% and about 5 wt% of one or more chelating agents;

between about 0.01 wt% and about 1 wt% of one or more corrosion inhibitors; and

a solvent.

40. The method of claim 39, wherein the at least one chelating agent is selected from the group consisting of glycine, ethylenediamine, ethylenediamine tetraacetate, citric acid, ammonium citrate, salts thereof, derivatives thereof, and combinations thereof, and the corrosion inhibitor is selected from the group consisting of benzotriazole, 5-methyl-1-benzotriazole, salts thereof, derivatives thereof, and combinations thereof.

41. The method of claim 40, wherein the corrosion inhibitor comprises benzotriazole and the at least one chelating agent comprises glycine or ethylenediamine and ammonium citrate.

42. The method of claim 41, wherein the second polishing composition further comprises polyethylene glycol.

43. The method of claim 39, wherein the second polishing composition further comprises at least one member selected from the group consisting of abrasive particulates, an oxidizer, at least one pH adjusting agent to provide a pH from about 4 to about 7, and combinations thereof.

44. The method of claim 39, wherein the polishing composition has a conductivity in a range from about 15 mS to about 40 mS.

45. The composition of claim 43, wherein the composition comprises:

between about 1% and about 5% by weight (wt.%) of a phosphoric acid based electrolyte in the total volume of solution;

between about 0.1% and about 5% by volume or weight of the one or more chelating agents in the total volume of solution;

between about 0.01% and about 1.0% by volume or weight of the one or more corrosion inhibitors in the total volume of solution;

between about 0.1% and about 5% by volume or weight of the one or more inorganic or organic acid salts in the total volume of solution;

between about 0.1% and about 25% by volume or weight of the pH adjusting agent in the total volume of solution to provide a pH of between about 4 and about 7;

between about 0.05% and about 5% by weight of abrasive particles in the total volume of solution; and

the remainder a solvent.

46. The composition of claim 45, further comprising between about 0.01% and about 3% by volume or weight of one or more oxidizers.

47. The composition of claim 45, wherein the composition comprises:

about 1.5% by volume phosphoric acid;

about 0.4% by volume ethylenediamine;

about 0.25% by weight benzotriazole;

about 0.8% by weight ammonium citrate;

between about 0.5% and about 3% by volume of 40% potassium hydroxide solution to provide a pH of about 5.4;

about 0.7% by weight of silica abrasives; and

deionized water.

48. The composition of claim 47, further comprising about 0.5% by volume of hydrogen peroxide.

49. The composition of claim 1, wherein the composition comprises:

between about 0.6% and about 1 % by volume of phosphoric acid;

about 0.5% and about 2% by volume of glycine;

about 0.35% by weight benzotriazole;

about 2% by weight ammonium citrate;

between about 0.5% and about 3% by volume of potassium hydroxide to provide a pH between about 4.9 and about 6.1;

about 0.5% by volume of hydrogen peroxide;

about 0.7% by weight of silica abrasives; and

deionized water.

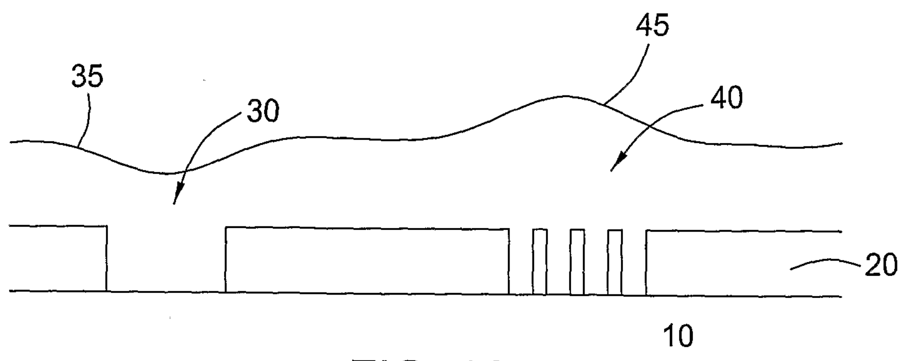


FIG. 1A
(PRIOR ART)

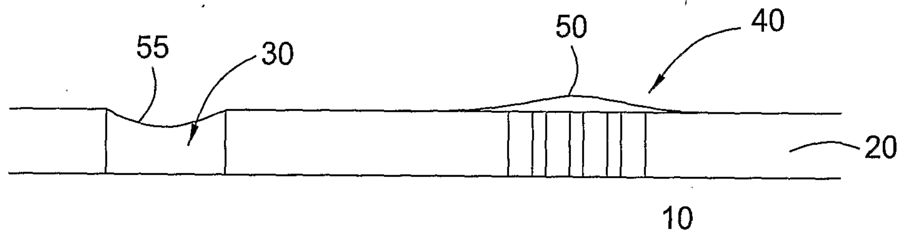


FIG. 1B
(PRIOR ART)

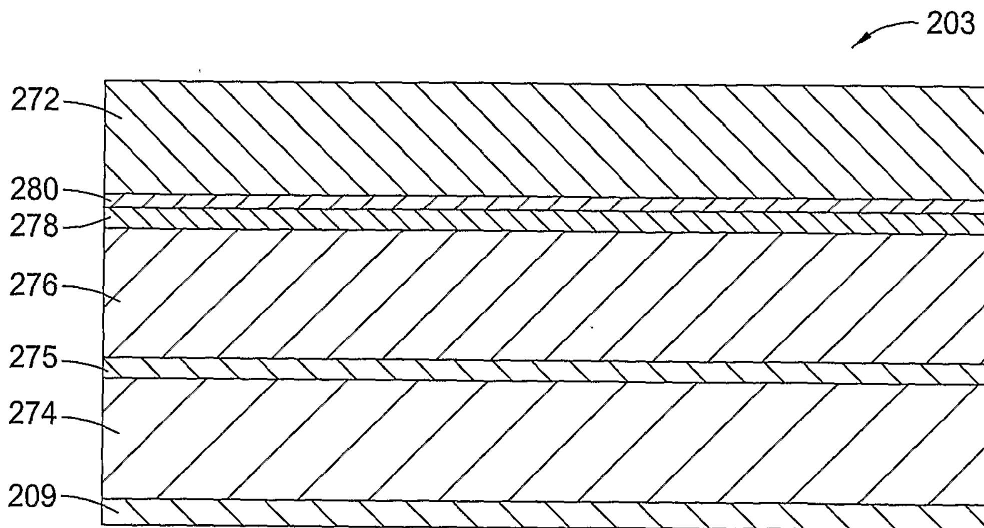


FIG. 3A

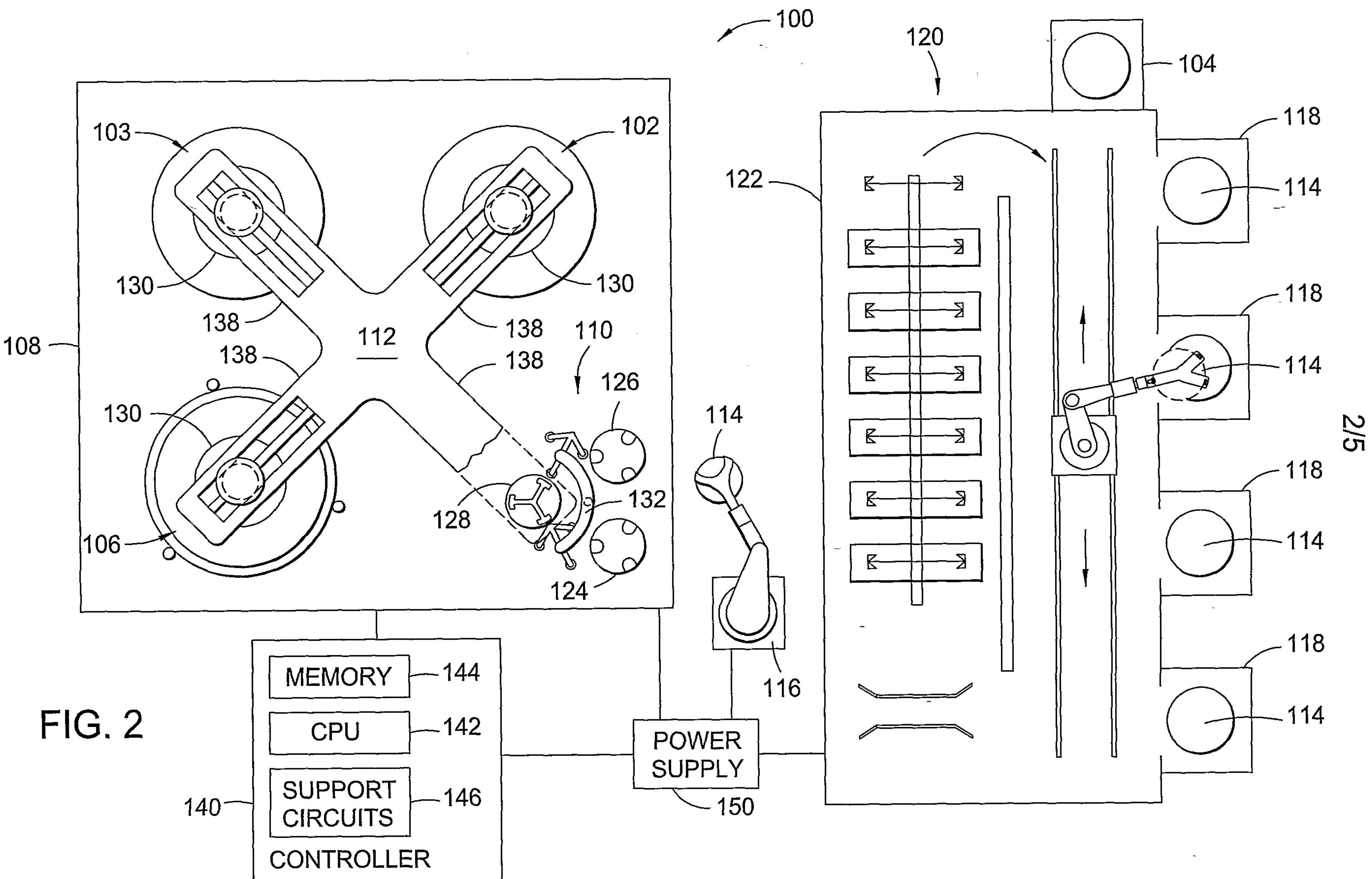


FIG. 2

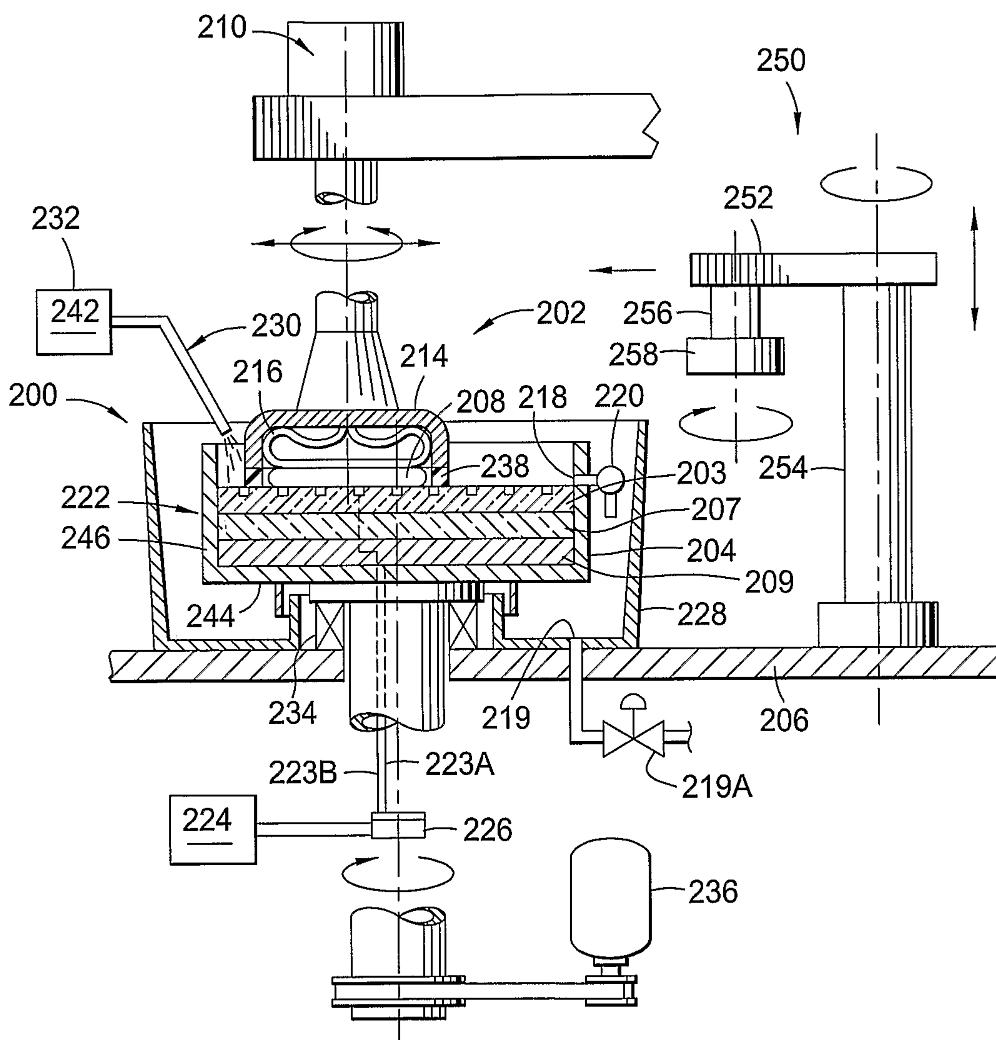


FIG. 3

FIG. 4A

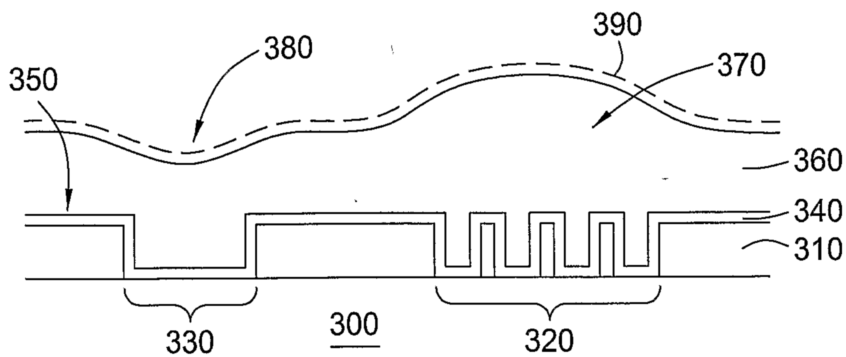


FIG. 4B

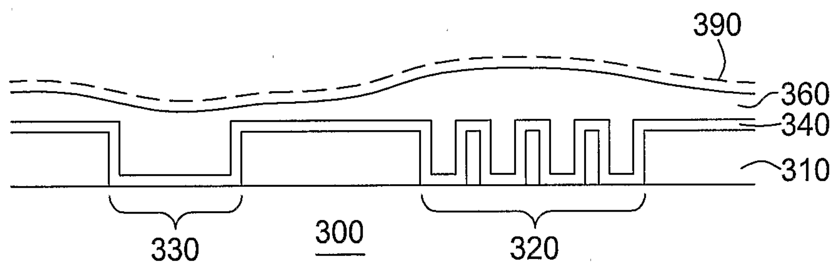


FIG. 4C

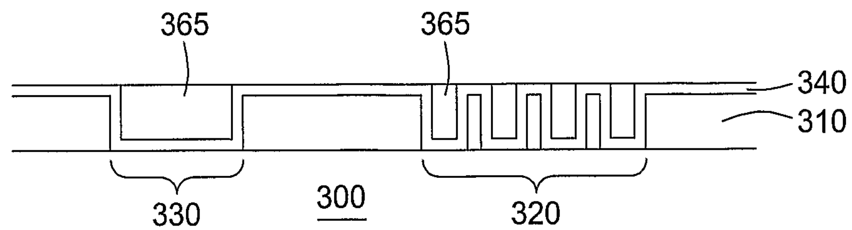


FIG. 4D

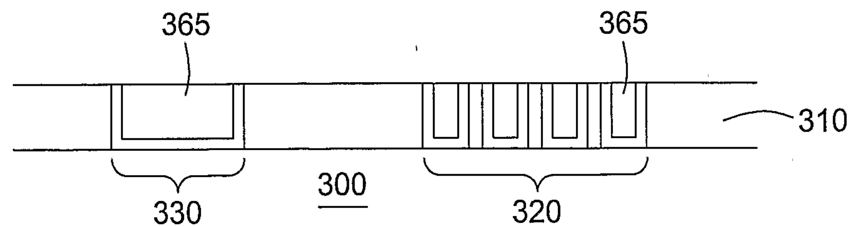


FIG. 5A

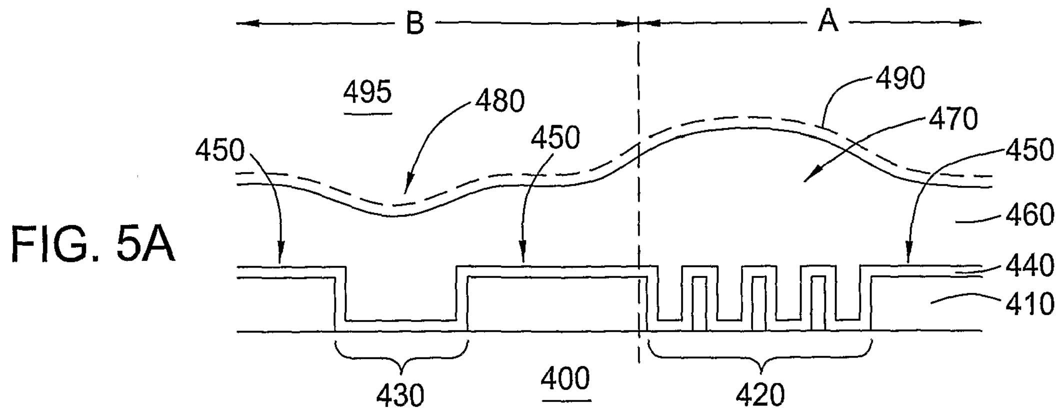


FIG. 5B

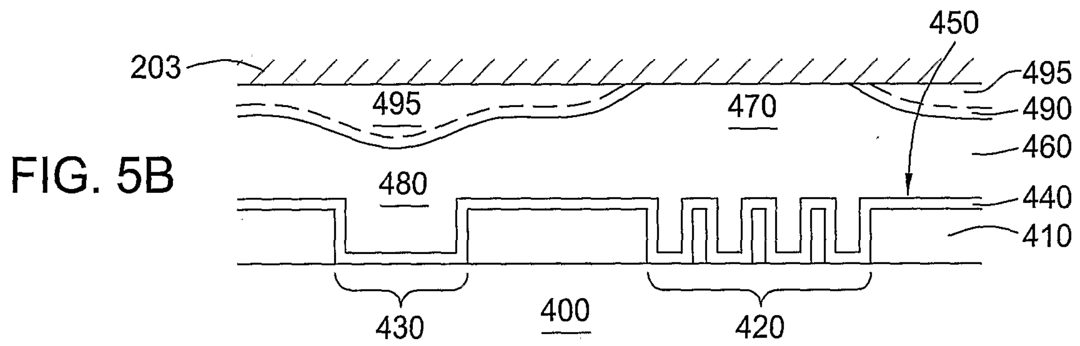


FIG. 5C

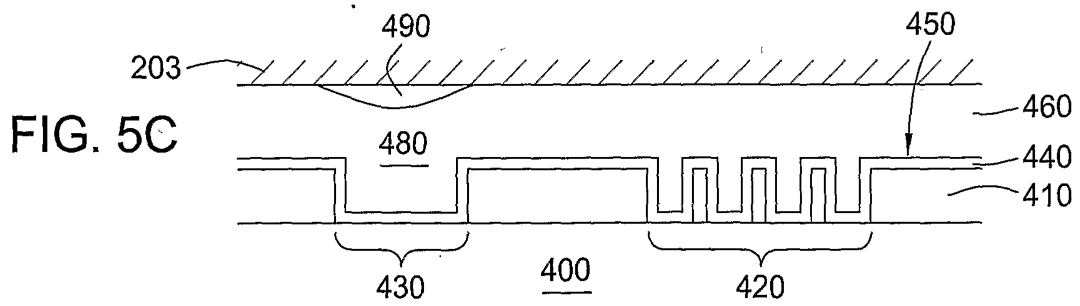


FIG. 5D

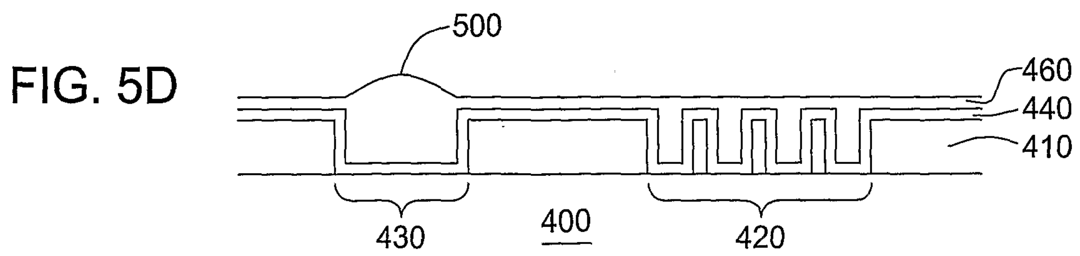
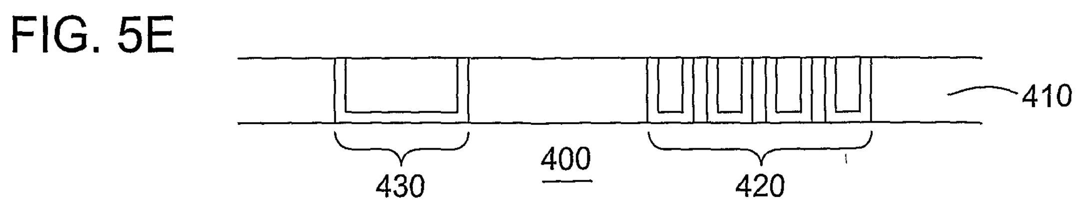


FIG. 5E



INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/017691

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09G1/02 C09K3/14 H01L21/3213 C09G1/02 H01L21/321
B23H5/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09G H01L B23H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 2002/104764 A1 (BANERJEE GAUTAM ET AL) 8 August 2002 (2002-08-08) paragraphs '0007! - '0009!, '0020!, '0023!, '0026! - '0030!, '0034!; figures 3,4	1-5,7,9, 12,17 20-26, 29,34
Y	US 2003/073311 A1 (LEVERT JOSEPH ET AL) 17 April 2003 (2003-04-17) paragraphs '0022!, '0055!; table 1	20-26, 29,34
X	WO 01/77241 A (APPLIED MATERIALS INC) 18 October 2001 (2001-10-18) page 6, lines 11-29; claims 1-6	39,40, 44-46
X,P	WO 03/072672 A (APPLIED MATERIALS INC) 4 September 2003 (2003-09-04) claims	39-41, 44-46
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
9 November 2004	16/11/2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Girard, Y

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International Application No
PCT/US2004/017691

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 2002/182982 A1 (LI JUI-LUNG ET AL) 5 December 2002 (2002-12-05) paragraphs '0054!, '0059! - '0061!	39,40

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