A method and an apparatus for electrochemically removing a metal from a substrate surface with an electrolyte and an electrode that has a surface defining a shape suitable to cause substantially uniform removal of a metal-containing surface.
SYSTEMS FOR ELECTROLYTIC REMOVAL OF METALS FROM SUBSTRATES

FIELD OF THE INVENTION

[0001] The present invention relates particularly to electrolytic removal (e.g., dissolution, etching, or polishing) methods for use in the formation of various structures on substrates, such as semiconductor substrates or substrate assemblies.

BACKGROUND OF THE INVENTION

[0002] Films of metals and metal oxides, particularly the heavier elements of Groups 8-11 (Fe, Co, Ni, and Cu groups), are becoming important for a variety of electronic applications. This is at least because many of the Group 8-11 metal films (e.g., Pd, Pt) are generally unreactive, resistant to oxidation or retard the diffusion of oxygen, and are good conductors. Oxides of certain of these metals also possess many of these properties, although perhaps to a different extent.

[0003] Thus, films of Group 8-11 metals, their alloys, and metal oxides, particularly the second and third row metals (e.g., Ru, Os, Rh, Ir, Pd, and Pt) have suitable properties for a variety of uses in integrated circuits. For example, they can be used in integrated circuits for barrier materials, for example. They are particularly suitable for use as barrier layers between the dielectric material and the silicon substrate in memory devices. Furthermore, they are suitable as the plate (i.e., electrode) itself in capacitors.

[0004] Platinum is one of the candidates for use as an electrode for high dielectric capacitors. Capacitors are the basic charge storage devices in random access memory devices, such as dynamic random access memory (DRAM) devices, static random access memory (SRAM) devices, and now ferroelectric memory (FE RAM) devices. They consist of two conductors, such as parallel metal or polysilicon plates, which act as the electrodes (i.e., the storage node electrode and the cell plate capacitor electrode), insulated from each other by a dielectric material (a ferroelectric dielectric material for FE RAMs). Thus, there is a continuing need for methods for the processing, e.g., removal, of Group 8-11 metal-containing films, preferably, platinum-containing films.

[0005] The planarization of a surface that includes platinum and other Group 8-11 metals typically involves mechanical polishing, as opposed to chemical-mechanical polishing, because they are relatively chemically inert and/or have relatively few water soluble products. Such mechanical polishing uses alumina, silica, or other abrasive particles to remove the metal physically. Unfortunately, mechanical polishing tends to smear (e.g., deform) the metals, leaving metal over undesired portions of the wafer surface, and leaving scratches in either the metal itself or other areas on the wafer surface. Also, many commercially available abrasive slurries do not effectively planarize platinum or other Group 8-11 metal-containing surfaces either because no material is removed or the resultant surface has defects therein.

[0006] Various etching processes are used in the fabrication of semiconductor devices to remove various materials. Such etching processes are used to control and maintain critical dimensions of various device structures such as, for example, transistors, capacitors, and interconnects. However, the removal of materials such as Group 8-11 metal-containing films by wet etching, for example, is generally very difficult. This is particularly true with respect to films containing rhodium, iridium, alloys thereof, and oxides thereof. For example, removal of metallic rhodium (Rh) and iridium (Ir) requires the use of high temperatures and/or high pressures with strong oxidizers and acids.

[0007] Thus, a need still exists for methods of removal of materials, particularly metal-containing films, from semiconductor substrates or substrate assemblies, in a more uniform manner.

SUMMARY OF THE INVENTION

[0008] The present invention provides systems and methods that overcome many of the problems associated with the removal of metals from substrates. Preferably, the systems and methods of the present invention are effective for the removal of at least one metal (which is used herein to include metalloids or semimetals) from a surface. Such a surface is referred to herein as a "metal-containing surface." That is, a "metal-containing surface" refers to an exposed region having a metal present that is to be removed. In such an exposed region, the metal is preferably present in an amount of at least about 10 atomic percent, preferably at least about 20 atomic percent, and most preferably at least about 50 atomic percent, of the composition of the region, which may be provided as a layer, film, coating, etc., to be etched in accordance with the present invention. The surface preferably includes one or more metals in elemental form or an alloy thereof (with each other and/or one or more other metals of the Periodic Table), as well as conductive oxides and silicides thereof. More preferably, the surface includes (and most preferably, consists essentially of) one or more metals in elemental form or an alloy of such metals only.

[0009] In one embodiment of the present invention, there is provided an apparatus for electrochemically removing a metal from a substrate surface with an electrolyte. The apparatus includes: a reservoir for containing the electrolyte; a first electrode comprising a substrate having a metal-containing surface positioned to interface with the electrolyte; and a counter electrode in electrical contact with the first electrode, wherein the counter electrode has a surface defining a shape suitable to cause substantially uniform removal of the metal-containing surface. Herein "substantially uniform" removal means the constant removal or material across a substrate surface (e.g., wafer surface) within 1%.

[0010] The counter electrode shape can be conical, partial conical, convex, or semi-parabolic shape, for example. The counter electrode can define two or more of the shapes suitable to cause substantially uniform removal of the metal-containing surface. For example, the two or more of the shapes comprise two or more concentrically arranged ridges, which can form concentric rings. Alternatively, the counter electrode can define a concentrically arranged continuous ridge. In addition, the counter electrode can have a surface defining two or more electrically isolated areas, where each electrically isolated area can deliver alternating or bipolar electrical current suitable to cause substantially uniform removal of the metal-containing surface. The counter elec-
trode and/or the two or more electrically isolated areas, can be defined also by its cross-sectional shape. For example, the counter electrode can have a triangular cross-sectional shape or a semi-circular cross-sectional shape.

[0011] The present invention also provides a method for electrochemically removing a metal from a substrate surface with an electrolyte. The method includes: providing an electrochemical cell that includes: a reservoir for containing an electrolyte; a first electrode comprising a substrate having a metal-containing surface positioned to interface with the electrolyte; and a counter electrode in electrical contact with the first electrode, wherein the counter electrode has a surface defining a shape suitable to cause substantially uniform removal of the metal-containing surface; and applying an alternating or bipolar pulsed electrical current to the electrochemical cell. Alternatively, the counter electrode can have a surface defining two or more electrically isolated areas, where each electrically isolated area can be used to deliver alternating or bipolar electrical current suitable to cause substantially uniform removal of the metal-containing surface.

[0012] As used herein, “semiconductor substrate or substrate assembly” refers to a semiconductor substrate such as a base semiconductor layer or a semiconductor substrate having one or more layers, structures, or regions formed thereon. A base semiconductor layer is typically the lowest layer of silicon material on a wafer or a silicon layer deposited on another material, such as silicon on sapphire. When reference is made to a substrate assembly, various process steps may have been previously used to form or define regions, junctions, various structures or features, and openings such as capacitor plates or barriers for capacitors.

BRIEF DESCRIPTION OF THE FIGURES

[0013] FIG. 1 is a schematic of an example of an electrolytic etching apparatus according to the present invention.

[0014] FIG. 2 is a schematic of a shaped electrode suitable for use in an electrolytic etching apparatus of the present invention.

[0015] FIGS. 3A-3E are schematics of various planar electrodes suitable for use in an electrolytic etching apparatus of the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0016] The present invention provides systems and methods of removing a metal from a surface electrolytically, as by etching or dissolving, for example, particularly a surface that includes one or more metals such as platinum, for example. Any of the metals of the Periodic Table can be removed using the systems and methods of the present invention. This includes main group metals, transition metals, lanthanides, actinides, as well as metalloids (i.e., semi-metals) such as aluminum and silicon. The term “metal” herein is used to include all of these.

[0017] Although the invention is not limited by the metal to be removed, the invention is described herein in terms of removing one or more of the Group VIIIIB metals (i.e., Groups 8, 9, and 10) and Group IB metals (i.e., Group 11) from a surface. More preferably, the methods of the present invention are effective for the removal of at least one of Co, Rh, Ru, Ir, Ni, Pd, Pt, Os, Au, and Ag from a surface. Most preferably, the methods of the present invention are effective for the removal of at least one of Rh, Ir, Pt, or alloys thereof, from a surface. Such a surface is referred to herein as a “metal-containing surface” (this preferably refers to those containing second and/or third row transition metals).

[0018] Herein, a “metal-containing surface” includes an exposed region having a metal present. In such an exposed region, the metal is preferably present in an amount of at least about 10 atomic percent, more preferably at least about 20 atomic percent, and most preferably at least about 50 atomic percent, of the composition of the region, which may be provided as a layer, film, coating, etc., to be processed in accordance with the present invention. In addition, the metal-containing surface can further include one or more of a conductive oxide, silicide, or combination thereof.

[0019] The process of the present invention includes electrochemically removing a metal. This typically includes electrochemical dissolution and is often referred to generically as electroetching or electrolytic etching.

[0020] Electrolytic etching, i.e., electroetching, is one of the number of methods commonly used to remove metals from the surface of a metallic workplace (i.e., a substrate) to provide the workplace with an etched surface layer. Typically, in the electroetching method, the surface to be etched forms the anode of an electrolytic cell and a counter electrode (i.e., the cathode) is appropriately positioned to complete the cell. A suitable electrolyte is then directed onto the metal surface (i.e., the anode) while an electric current is applied to the system, leading to an accelerated etching of the metallic surface.

[0021] Typically, when electroetching noble metals a direct current process seems to be self-passivate, and stops etching after a short period of time, often as short as several seconds. However, if an alternating current is applied, then the etch process can continue until the metal layer is consumed. In addition, a bipolar pulsed current could be used in place of an alternating current.

[0022] In the microelectronics industry, electroetching is commonly used for through-mask patterning and for the removal of a continuous thin film of conducting metal (such as seed layers) from the surface of a semiconductor wafer. Different types of electroetching apparatus are known, and the literature describes a variety of electrolyte flow systems for use with such apparatus ranging from non-agitated to impinging electrolyte jets. For example, electroetching systems are known that progressively treat only a small portion of the wafer to be etched using a multi-nozzle cathode assembly that has a small width relative to the overall dimensions of the wafer (surface) to be etched.

[0023] A preferred process of the present invention involves electropolishing. This is a type of planarization, and is often considered an alternative to chemical mechanical polishing (CMP). Electropolishing is a method of polishing metal surfaces by applying an electric current through an electrolytic bath using, for example, a conductive pad.
Any of a wide variety of systems can be used for the methods of the present invention. The following description provides a general description of the electropolishing process. It is appreciated that changes to any number of apparatus components and/or operating conditions can be made without departing from the overall electropolishing process.

FIG. 1 shows an apparatus 10 for electrochemically etching a surface 12 of a substrate, such as the wafer 14. The apparatus 10 generally includes a reservoir 11, which is preferably made of a plastic material to resist the corrosive effects of the electrolyte used in the process. The reservoir 11 is typically adapted with a holder (not shown) for receiving the wafer 14 from which material is to be electrolytically removed, e.g., etched. The wafer 14 is preferably positioned within the holder so that the wafer 14 is placed with the metallized side (the surface 12) exposed to the electrolyte and held in place such that there it is electrically connected to form a first electrode of an electrochemical etching circuit. The etching circuit further includes a power supply 22.

The counter electrode 30 preferably has a surface that includes a configuration and a shape designed to generate substantially uniform removal of metal from the surface 12. In one preferred embodiment, essentially the entire surface of the counter electrode 30 is configured to define the shape of the electrode 30. In other words, the surface of the electrode 30 is configured into a single shape. Preferably, the surface of the counter electrode 30 defines a non-planar shape such as a conical, a partial conical, or a convex (dome-shaped) shape.

In addition, other non-planar surface shapes that provide for substantially uniform removal of metal from the surface are also possible. In one embodiment, the counter electrode 30 can include two or more examples of concentrically arranged shapes. An example is shown in FIG. 2, where the counter electrode 30 can include concentrically arranged ridges, or rings, 60 that provide a surface designed to generate substantially uniform removal. Preferably, the ridges can be continuous (as shown in FIG. 2) or non-continuous, (e.g., a non-uniform ridge height). Preferably, the ridges can also have a cross-sectional shape that includes triangular, semi-circular, and semi-parabolic. Other cross-sectional shapes are also possible.

Although the shape shown in FIG. 1 for the counter electrode is particularly desirable, it is not required. For example, the counter electrode can be in any shape or size as long as it is made of a material, such as stainless steel, that completes the electrochemical circuit and facilitates removal of material from the first electrode. Other materials of which the counter electrode can be made include, for example, Pt, Ni and/or Au. In addition, it is possible to have two or more counter electrodes.

In an additional embodiment, the surface of the counter electrode can include structures that define two or more electrically isolated areas. In this example, each electrically isolated area can deliver electricity suitable to cause substantially uniform removal of the metal-containing surface. FIGS. 3A-3E provide schematic examples of counter electrodes that include two or more electrically isolated areas suitable for use in the electrolytic etching apparatus of the present invention.

The counter electrode 30 typically includes a surface 100 that defines a planar shape. Other shapes, as described herein, are also possible (e.g., non-planar). The surface 100 can be divided so as to define two or more electrically isolated areas 110. In one example, the surface 100 is divided by electrical insulators 120 suitable to electrically isolate the areas 110 from each other.

Each of the electrically isolated areas 110 are electrically coupled to the power supply, where the term power supply includes one or more power supplies. Preferably, the power supply can be used to provide electricity having the same and/or different voltage values and/or frequency values to any of the or more electrically isolated areas 110. In addition, the power supply can be used to provide electricity having different waveforms to any of the two or more electrically isolated areas 110. For example, the power supply can be used to provide waveforms having variable pulse widths and duty cycles, variable pulse heights between positive and negative polarity, or any combination thereof, to any of the two or more electrically isolated areas 110. Preferably, the power supply delivers alternating or pulsed bipolar electric current between any of the two or more electrically isolated areas 110 of the counter electrode 30 and the first electrode.

In one example, the power supply can be used to deliver at least a first alternating or pulsed bipolar electric current between the first electrode and one of the two or more electrically isolated areas 110. At the same time, or at a different time, the power supply can be used to deliver a second alternating or pulsed bipolar electric current between the first electrode and another of the two or more electrically isolated areas 110, where the first and second alternating or pulsed bipolar electric current have the same or different electrical properties, as discussed above.

As FIGS. 3A-3B illustrate, there can be many electrically isolated areas 110 of the counter electrode 30, where each of the areas 110 can be used to deliver electricity having one or more of the same and/or different electrical properties, as discussed above. In addition, all or fewer than all of the electrically isolated areas 110 can be used in delivering the electrical current as described.

As discussed above, the two or more electrically isolated areas 110 define at least one shape suitable to cause substantially uniform removal of the metal-containing surface. For example, the two or more electrically isolated areas 110 can be concentrically arranged on the surface 100. FIG. 3A provides an example of concentrically arranged areas 110, where the areas 110 from concentric rings. Alternatively, areas 110 having other shapes and arrangements on the surface 100 can also be used. FIG. 3B provides one such example, where the areas 10 have a circular shape and are arranged in a repeating pattern on the surface 100. As will be appreciated, other shapes, or combination of shapes could be used to define areas 110 in repeating or non-repeating patterns. In addition, the surface 100 can include greater or fewer areas 10 than are shown in FIG. 3A or 3B. In other words, the percentage of the total area occupied by the areas 110 on the surface 100 can be greater or less than is shown in FIGS. 3A and 3B.

As discussed above, the surface 100 of counter electrode 30 can define additional shapes. FIGS. 3C-3E provide examples where surface 100 defines additional
shapes (e.g., non-planar shapes) that provide for substantially uniform removal of metal from the surface. The counter electrode 30 can include concentrically arranged ridges, or rings, 60 that provide a surface designed to generate substantially uniform removal. Preferably, the ridges can be continuous (as shown in FIGS. 3C-3E) or non-continuous, (e.g., a non-uniform ridge height). Preferably, the ridges can also have a cross-sectional shape that includes triangular (FIG. 3C), semi-circular (FIG. 3D), and semi-parabolic (FIG. 3E). Other shapes, number of shapes, combination of shapes, spacing of the shapes, sizes of shapes (including the relative size of the shapes) are also possible.

[0036] Referring again to FIG. 1, a suitable electrolyte can be delivered and caused to impinge upon the surface 12 of the wafer 14 by any of a variety of mechanisms. Such mechanisms are well known in the art. For example, impinging electrolyte jets could be used to direct the electrolyte to the surface 12. Alternatively, an electrolyte bath can be used to expose the surface 12 to the electrolyte. Examples of mechanisms for delivering electrolyte are illustrated in U.S. Pat. Nos. 6,234,870 to Uzoh et al.; 6,103,096 to Datta et al.; 6,083,376 to Akram et al.; 5,614,076 to Brophy et al.; and 5,256,565 to Bernhardt et al.

[0037] The electrolyte is preferably an aqueous solution that includes one or more components that makes the solution electrically conductive. Also, the metal being removed should form a soluble salt in the electrolyte. Preferably, the electrolyte also chemically enhances removal of the desired material relative to the material that is not to be removed. Examples of suitable electrolytes include aqueous solutions of hydrochloric acid, ammonium hydroxide, acetic acid, and/or other dilute mineral acids such as sulfuric acid, and/or phosphoric acid. A preferred electrolyte is hydrochloric acid.

[0038] The concentration of the electrolyte is preferably sufficient to provide electrical conductivity, and preferably, enhance removal of the desired material. Preferably, the electrolyte concentration is within a range of about 0.01 moles per liter of solution (Molar) to about 12 Molar. More preferably, the electrolyte concentration is within a range of about 1.0 Molar to about 3.0 Molar. In addition, it is also possible to add one or more salts at a concentration sufficient to enhance the conductivity of the electrolyte solution.

[0039] The spacing, or interelectrode gap, between the workpiece (i.e., the wafer 14), which serves as one electrode, and the counter electrode 30, is preferably kept small to maintain effective electrolyte impingement and to allow the cell voltage to be kept as low as possible. For example, an interelectrode gap of about 0.1 millimeter (mm) to about 5 mm is preferred because a larger gap will tend to require a higher cell voltage while a lower gap will tend to yield stronger edge effects.

[0040] The wafer 14 and/or the counter electrode 30 can be attached to a shaft and motor (not shown) for providing rotational motion. This embodiment draws upon the concept of rotating disc electrodes and can be designed according to well known techniques.

[0041] Typically, a mask layer is patterned over the layer of material to be removed by the electrolytic process of the present invention. The masking is accomplished with a material of relatively low ionic conductivity and diffusivity, which effectively slows or blocks transport of the metal ions produced during electrolytic removal.

[0042] The apparatus 10 can also be modified to include rinsing and drying functions. Alternatively, the etching, rinsing, and drying functions can also be performed using three separate stations. An appropriate mechanism, such as a robot, for example, can carry the substrate, such as the wafer 14, among three separate stations. The substrate is etched at a first station, rinsed at a second station, and dried at a third station.

[0043] The counter electrode 30 and wafer 14 are electrically connected to a voltage source or power supply 22. The current and voltage of the electrolytic system will depend on the cell design and the desired rate of removal. Generally, direct currents only work if no more than a few angstroms of material are to be removed. Typical currents are within a range of about 0.001 to about 40 Amperes. Typical voltages are within a range of about 1 to about 100 volts. Generally, the higher the current, the higher the rate of material removal. Preferably, a method in accordance with the present invention is conducted at atmospheric pressure and at a temperature of about 10° C. to about 100° C., and more preferably at a temperature of about 10° C. to about 60° C.

[0044] Removal of material in such an electrolytic system may introduce a certain degree of roughness to the surface 12 of the wafer 14 due to the inability of the process to provide micro-smooth surfaces. Thus, the electrolytic etching process can be followed by a chemical mechanical polishing (CMP) process to remove the surface roughness if desired. CMP may also aid in the removal of thin electrically isolated areas from the surface 12 of the wafer 14. Herein, “chemical mechanical polishing” and “CMP” refer to a dual mechanism having both a chemical component and a mechanical component, wherein corrosion chemistry and fracture mechanics both play a roll in the removal of material, as in wafer polishing. An example of such a process is described in Applicants’ Assignee’s COPING System and methods for the electrolytic removal of Metals from Substrates (Attorney Docket No. 150.01120101).

[0045] The foregoing detailed description has been given for clarity of understanding only. No unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described, for variations obvious to one skilled in the art will be included within the invention defined by the claims. For example, while the description above focused on planarization of semiconductor-based substrates, the compositions and methods of the invention are also applicable to, for example, polishing metallic mirrors, as one of many other possible applications. The complete disclosures of all patents, patent documents, and publications listed herein are incorporated by reference, as if each were individually incorporated by reference.

What is claimed:
1. An apparatus for electrochemically removing a metal from a substrate surface with an electrolyte, comprising:
a reservoir for containing the electrolyte;

a first electrode comprising a substrate having a metal-containing surface positioned to interface with the electrolyte; and

a counter electrode in electrical contact with the first electrode;

wherein the counter electrode has a surface defining a shape suitable to cause substantially uniform removal of the metal-containing surface.

2. The apparatus of claim 1 wherein the surface of the counter electrode defines a conical shape.

3. The apparatus of claim 1 wherein the surface of the counter electrode defines a partial conical shape.

4. The apparatus of claim 1 wherein the surface of the counter electrode defines a convex shape.

5. The apparatus of claim 1 wherein the surface of the counter electrode defines two or more of the shapes suitable to cause substantially uniform removal of the metal-containing surface.

6. The apparatus of claim 5 wherein the two or more of the shapes comprise two or more concentrically arranged ridges.

7. The apparatus of claim 6 wherein the two or more concentrically arranged ridges form concentric rings.

8. The apparatus of claim 6 wherein the surface of the counter electrode defines a triangular cross-sectional shape.

9. The apparatus of claim 6 wherein the surface of the counter electrode defines a semi-circular cross-sectional shape.

10. The apparatus of claim 6 wherein the surface of the counter electrode defines a semi-parabolic shape.

11. The apparatus of claim 1 wherein the surface of the counter electrode defines a concentrically arranged continuous ridge.

12. The apparatus of claim 1 wherein the counter electrode is made of a material comprising stainless steel.

13. The apparatus of claim 1 wherein the metal-containing surface comprises a metal selected from the group consisting of a Group 8-10 metal and a combination thereof.

14. The apparatus of claim 13 wherein the substrate is a semiconductor substrate or substrate assembly.

15. The apparatus of claim 14 wherein the substrate is a silicon wafer.

16. The apparatus of claim 1 wherein the metal-containing surface comprises a metal selected from the group consisting of a Group 8-10 metal and a combination thereof.

17. The apparatus of claim 16 wherein the substrate is a semiconductor substrate or substrate assembly.

18. The apparatus of claim 17 wherein the substrate is a silicon wafer.

19. The apparatus of claim 1 further comprising a power supply to deliver alternating or pulsed bipolar electric current between the first electrode and the counter electrode.

20. The apparatus of claim 19 wherein the power supply delivers alternating current with a voltage in a range of about 1 to about 100 volts.

21. The apparatus of claim 19 wherein the power supply delivers alternating current with a current in a range of about 0.001 to about 40 Amperes.

22. A method for electrochemically removing a metal from a substrate surface with an electrolyte, the method comprising:

providing an electrochemical cell comprising:

a reservoir for containing an electrolyte;

a first electrode comprising a substrate having a metal-containing surface positioned to interface with the electrolyte; and

a counter electrode in electrical contact with the first electrode;

wherein the counter electrode has a surface defining a shape suitable to cause substantially uniform removal of the metal-containing surface; and

applying an electrical current to the electrochemical cell.

23. The method of claim 22 wherein the surface of the counter electrode defines a conical shape.

24. The method of claim 22 wherein the surface of the counter electrode defines a partial conical shape.

25. The method of claim 22 wherein the surface of the counter electrode defines a convex shape.

26. The method of claim 22 wherein the surface of the counter electrode defines two or more of the shapes suitable to cause substantially uniform removal of the metal-containing surface.

27. The method of claim 26 wherein the two or more of the shape comprise two or more concentrically arranged ridges.

28. The method of claim 27 wherein the two or more concentrically arranged ridges form concentric rings.

29. The method of claim 27 wherein the surface of the counter electrode defines a triangular cross-sectional shape.

30. The method of claim 27 wherein the surface of the counter electrode defines a semi-circular cross-sectional shape.

31. The method of claim 28 wherein the surface of the counter electrode defines a semi-parabolic shape.

32. The method of claim 22 wherein the surface of the counter electrode defines a concentrically arranged continuous ridge.

33. The method of claim 22 wherein the counter electrode is made of a material comprising stainless steel.

34. The method of claim 22 wherein the metal-containing surface comprises a metal selected from the group consisting of a Group 8-10 metal and a combination thereof.

35. The method of claim 34 wherein the substrate is a semiconductor substrate or substrate assembly.

36. The method of claim 35 wherein the substrate is a silicon wafer.

37. The method of claim 22 wherein the metal-containing surface comprises a metal selected from the group consisting of a Group 8-10 metal and a combination thereof.

38. The method of claim 37 wherein the substrate is a semiconductor substrate or substrate assembly.

39. The method of claim 38 wherein the substrate is a silicon wafer.

40. The method of claim 22 further comprising delivering alternating or pulsed bipolar electric current between the first electrode and the counter electrode.

41. The method of claim 40 further comprising delivering alternating current with a voltage in a range of about 1 to about 100 volts.

42. The method of claim 40 further comprising delivering alternating current with a current in a range of about 0.001 to about 40 Amperes.

43. An apparatus for electrochemically removing a metal from a substrate surface with an electrolyte, comprising:
a reservoir for containing the electrolyte;

a first electrode comprising a substrate having a metal-containing surface positioned to interface with the electrolyte; and

a counter electrode in electrical contact with the first electrode;

wherein the counter electrode has a surface defining two or more electrically isolated areas, wherein each electrically isolated area delivers alternating or bipolar electrical current suitable to cause substantially uniform removal of the metal-containing surface.

44. The apparatus of claim 43 wherein the surface of the counter electrode defines a planar shape.

45. The apparatus of claim 44 wherein the two or more electrically isolated areas are concentrically arranged on the planar shape.

46. The apparatus of claim 45 wherein the two or more electrically isolated areas form concentric rings.

47. The apparatus of claim 44 wherein the two or more electrically isolated areas define at least one shape suitable to cause substantially uniform removal of the metal-containing surface.

48. The apparatus of claim 43 wherein the power supply delivers at least a first alternating or pulsed bipolar electric current between the first electrode and one of the two or more electrically isolated areas and a second alternating or pulsed bipolar electric current between the first electrode and another of the two or more electrically isolated areas.

49. The apparatus of claim 48 wherein the power supply delivers the first and second alternating or pulsed bipolar electric current at different voltages.

50. The apparatus of claim 48 wherein the power supply delivers the first and second alternating or pulsed bipolar electric current at different frequencies.

51. The apparatus of claim 48 wherein the power supply delivers alternating current with a voltage in a range of about 1 to about 100 volts.

52. The apparatus of claim 48 wherein the power supply delivers alternating current with a current in a range of about 0.001 to about 40 Amperes.

53. The apparatus of claim 48 wherein the substrate is made of a material comprising stainless steel.

54. The apparatus of claim 43 wherein the metal-containing surface comprises a metal selected from the group consisting of a Group 8-11 metal and a combination thereof.

55. The apparatus of claim 54 wherein the substrate is a semiconductor substrate or substrate assembly.

56. The apparatus of claim 55 wherein the substrate is a silicon wafer.

57. The apparatus of claim 56 wherein the substrate is a silicon wafer.

58. The apparatus of claim 43 wherein the metal-containing surface comprises a metal selected from the group consisting of a Group 8-10 metal and a combination thereof.

59. The apparatus of claim 58 wherein the substrate is a semiconductor substrate or substrate assembly.

60. The apparatus of claim 59 wherein the substrate is a silicon wafer.

61. A method for electrochemically removing a metal from a substrate surface with an electrolyte, the method comprising:

providing an electrochemical cell comprising:

a reservoir for containing an electrolyte;

a first electrode comprising a substrate having a metal-containing surface positioned to interface with the electrolyte; and

a counter electrode in electrical contact with the first electrode;

wherein the counter electrode has a surface defining two or more electrically isolated areas, wherein each electrically isolated area delivers alternating or bipolar electrical current suitable to cause substantially uniform removal of the metal-containing surface; and

applying alternating or bipolar electrical current to the electrochemical cell.

62. The method of claim 61 wherein the surface of the counter electrode defines a planar shape.

63. The method of claim 62 wherein the two or more electrically isolated areas are concentrically arranged on the planar shape.

64. The method of claim 63 wherein the two or more electrically isolated areas form concentric rings.

65. The method of claim 62 wherein the two or more electrically isolated areas define at least one shape suitable to cause substantially uniform removal of the metal-containing surface.

66. The method of claim 62 wherein a power supply delivers at least a first alternating or pulsed bipolar electric current between the first electrode and one of the two or more electrically isolated areas and a second alternating or pulsed bipolar electric current between the first electrode and another of the two or more electrically isolated areas.

67. The method of claim 66 wherein the power supply delivers the first and second alternating or pulsed bipolar electric current at different voltages.

68. The method of claim 67 wherein the power supply delivers the first and second alternating or pulsed bipolar electric current at different frequencies.

69. The method of claim 67 wherein the power supply delivers alternating current with a voltage in a range of about 1 to about 100 volts.

70. The method of claim 66 wherein the power supply delivers alternating current with a current in a range of about 0.001 to about 40 Amperes.

71. The method of claim 66 wherein the substrate is made of a material comprising stainless steel.

72. The method of claim 61 wherein the metal-containing surface comprises a metal selected from the group consisting of a Group 8-11 metal and a combination thereof.

73. The method of claim 72 wherein the substrate is a semiconductor substrate or substrate assembly.

74. The method of claim 73 wherein the substrate is a semiconductor substrate or substrate assembly.

75. The method of claim 74 wherein the substrate is a silicon wafer.

76. The method of claim 75 wherein the metal-containing surface comprises a metal selected from the group consisting of a Group 8-10 metal and a combination thereof.

77. The method of claim 76 wherein the substrate is a semiconductor substrate or substrate assembly.

78. The method of claim 77 wherein the substrate is a silicon wafer.

* * * *