

FORMING AN OXIDE LAYER ON A FLAT CONDUCTIVE SURFACE

BACKGROUND OF THE INVENTION

1. Field of Invention

5 The present invention generally relates to forming an oxide layer on flat conductive surfaces such as surfaces of semiconductor devices and photovoltaic (PV) cells.

2. Description of Related Art

10 Photovoltaic (PV) cells, and more particularly, crystalline silicon photovoltaic cells typically have a front side surface operable to receive light and a back side surface opposite the front side surface. The front side surface is part of an emitter of the PV cell and has a plurality of electrical contacts formed therein and the back side surface has at least one electrical contact. The electrical contacts on the front and back side surfaces are used to connect the PV cell to an external electrical circuit.

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To improve PV cell efficiency by decreasing light reflection, the front side surface may be treated by wet chemical texturing and deposition of an antireflective coating. The antireflective coating typically comprises optically transparent materials of about **80-100** nm in thickness having a refractive index of about **1.8-2.3**. Use of an antireflective coating and texturing can decrease initial light reflection from **38%** to **8-12%** on multi-crystalline PV cells and to **5-7%** on mono-crystalline PV cells. A corresponding gain in the photovoltaic cell efficiency results.

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For crystalline silicon solar cells the most common type of antireflective coating is SiN_4 deposited by means of Atmospheric Pressure Chemical Vapor Deposition (APCVD) or Plasma Enhanced Chemical Vapor Deposition (PECVD). Although practically all photovoltaic cell manufacturing companies use this type of antireflective coating, these deposition techniques require high temperatures of up to **700** °C, have high energy consumption and require expensive manufacturing equipment.

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SiN_4 antireflective coatings cannot be used for the production of amorphous silicon photovoltaic cells and some types of hetero-junction photovoltaic cells because these

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types of cells cannot withstand processing temperatures above **300 °C**. These types of photovoltaic cells use other types of antireflective coatings, such as conductive metal oxides including, for example, Zinc Oxide doped with Aluminum $\text{Al:Zn}_y\text{O}_x$, Indium Oxide doped with Fluorine $\text{F:In}_y\text{O}_x$, or Indium Oxide doped with Tin: $\text{In}_x\text{Sn}_y\text{O}_z$ (also known as ITO). Transparent conductive oxides have found widespread application in thin film photovoltaic cells and modules because they decrease light reflection, and assist in establishing low resistance electrical connections between current collecting metallization patterns and front or back side surfaces of PV cells.

Industrial deposition of conductive metal oxide antireflective coatings on temperature sensitive photovoltaic cells is normally performed using magnetron sputtering, evaporation, or chemical vapor deposition techniques. Although these techniques do not require high temperatures, they use expensive equipment and high vacuum processes, and only provide low production capacity and result in the waste of expensive materials.

By using SiN_4 as an antireflective coating, photovoltaic cell efficiency is increased as a result of lower light reflection and because of the built-in positive electric charge of the SiN_4 layer. This built-in charge reflects negative electric charges from the front surfaces of p-type crystalline photovoltaic cells which improves passivation due to decreased charge recombination. This improved passivation results in photovoltaic cell efficiency gain.

Passivation quality similar to that of SiN_4 may be achieved if an Al_2O_3 layer about **20-200 nm** in thickness having a built-in negative charge is deposited on the rear side of a p-type crystalline photovoltaic cell. This built-in negative charge reflects negative charges from the rear surface of the solar cell that are generated when the PV cell is under illumination. Aluminum oxide layers can be deposited by Atomic Layer Deposition (ALD) technologies as described by B. Hoex, J. Schmidt, P. Pohl, M. C. M. van de Sanden, and W. M. M. Kessels, in an article entitled "Silicon Surface Passivation by Atomic Layer Deposited Al_2O_3 JOURNAL OF APPLIED PHYSICS **104**, p. **044903-1 - 044903-12**, **2008**; and in an article by G. Dingemans, W. Beyer, M. C.

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M. van de Sanden, and W. M. M. Kessels, entitled "Hydrogen Induced Passivation of Si Interfaces by Al₂O₃ Films and SiO₂/Al₂O₃ Stacks", APPLIED PHYSICS LETTERS **97**, **152106** _2010 and by radio frequency magnetron sputtering as described by T.T. A. Li and A. Cuevas, in an article entitled "Role of Hydrogen in the Surface Passivation of Crystalline Silicon by Sputtered Aluminum Oxide; PROGRESS IN PHOTOVOLTAICS: RESEARCH AND APPLICATIONS, **2011**; **19:320–325**. Unfortunately these technologies are quite expensive and do not provide sufficient production capacity.

The passivation effect of an Al₂O₃ layer may be used to improve crystalline silicon photovoltaic cell efficiency if cost-efficient techniques and equipment can be developed and commissioned into mass production.

An efficient passivation of the crystalline silicon solar cell may be achieved by forming a silicon oxide (SiO₂) passivation layer to have a thickness of about **10** nm to **20** nm on the front and/or rear surfaces of the solar cell. Efficient passivation occurs due to the strong reduction of the Si interface defect density. The SiO₂ passivation layer may be formed by thermal methods at very high temperatures (~**1050** °C) or through the use of wet oxidation processes with H₂O at ~**800** °C in wet atmosphere environment such as described by G. Dingemans, M. C. M. van de Sanden, and W. M. M. Kessels, in an article entitled "Excellent Si Surface Passivation by Low Temperature SiO₂ using an Ultrathin Al₂O₃ Capping Film", Phys. Status Solidi RRL **5**, No. **1**, **22–24** (**2011**). Unfortunately these processes are expensive, consume a large amount of energy and do not facilitate great accuracy in the production of the SiO₂ layer to a desired thickness and uniformity. Many efforts have been undertaken to avoid the long processing times and the very high temperatures (~**1050** °C) required for thermal SiO₂ formation, to prevent deterioration of the Si bulk quality. However, to date, the best surface passivation performance can be obtained by low temperature alternatives such as nitric acid oxidation (NAOS) and chemical vapour deposition (CVD) which produce considerably poorer quality SiO₂ layers and lower quality passivation than can be obtained with thermally-grown SiO₂.

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Alternative methods involve the use of electrochemical plating techniques to form metal oxide layers such as aluminum oxide, zinc oxide or indium oxide layers on semiconductor substrates.

5 US patent **6,346,184 B1** entitled "Method of Producing Zinc Oxide Thin Film, Method of Producing Photovoltaic Device and Method of Producing Semiconductor Device" to Masafumi Sano, Souraku-gun, Yuichi Sonoda describes a method of producing a zinc oxide thin film in which a current is passed between a conductive substrate immersed in an aqueous solution containing at least zinc ions and carboxylic acid ions, and an
10 electrode immersed in the aqueous solution to form a zinc oxide thin film on the conductive substrate. This method stabilizes formation of the zinc oxide thin film and improves adhesion between the thin film and the substrate. The zinc oxide film is deposited on a cathode comprising an optically transparent or non-transparent substrate coated with transparent conductive material such as indium oxide (In_2O_3),
15 indium tin oxide ($\text{In}_2\text{O}_3 + \text{SnO}_2$), zinc oxide (ZnO), or tin oxide (SnO_2) deposited by sputtering, vacuum deposition or chemical vapor deposition methods. The optically non-transparent conductive substrate on the cathode may be a flexible stainless steel film of **0.15** mm thickness coated with a silver and or conductive zinc oxide layer. The back side of the stainless steel film is covered with an electrically insulating film to
20 prevent electrochemical deposition of the zinc oxide layer thereon. Metallic foil could be used as a non - transparent conductive substrate. The patent discloses that a **4-N** purity zinc plate was used as the anode. The aqueous electrolyte solution described is an aqueous ammonia solution of zinc hydroxide, zinc oxalate or zinc oxide in concentrations of **0.001** to **3.0**mol/L and hydrogen ion exponent (pH) between a pH of
25 **8** and a pH of **12.5**.

US patent **6,110,347** entitled "Method for the Formation of an Indium Oxide Film by Electrodeposition Process or Electroless Deposition Process, a Substrate Provided with the Indium Oxide for a Semiconductor Element and a Semiconductor Element
30 Provided with the Substrate" to Kozo Arao, Nara; Katsumi Nakagawa; and Yukiko Iwasaki describes a method of producing an indium oxide film on an electrically conductive substrate by immersing the substrate and a counter electrode in an

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aqueous solution containing at least nitrate and indium ions and causing an electric current to flow between the substrate and the counter electrode, thereby causing an indium oxide film to form on the substrate. A film-forming method for the formation of an indium oxide on a substrate by an electroless deposition process, using the aqueous solution, and a substrate for a semiconductor element and a photovoltaic element produced using the film-forming method are further provided. In the process described, the negative cathode electrode can be made from any conductive metal or alloy. For example, the cathode may be a **0.12** mm thick stainless steel plate having a rear surface covered with insulating tape for protection against deposition of indium oxide thereon. The positive anode electrode may be made from a **0.2** mm thick platinum plate of **4-N** purity. The electrolyte may be an aqueous solution containing indium nitrate with sucrose or dextrin. Notably, the electrolyte must always be stirred by means of a magnetic agitator.

US patent **6,133,061** entitled "Method for Forming Thin Zinc Oxide Film, and Method for Producing Semiconductor Element Substrate and Photovoltaic Element Using Zinc Oxide Thin Film" to Yuichi Sonoda describes a method for forming a thin film of zinc oxide on a conductive substrate by electrode position from an aqueous solution, while preventing film deposition on the back surface of the substrate. More specifically, a film deposition-preventing electrode for preventing film deposition on the back surface of the substrate is provided in an aqueous solution containing nitrate ions, and a current is supplied such that the counter electrode is at a higher potential than the substrate which is at a higher potential than the film deposition-preventing electrode. This method can be applied to a process for preparing a solar cell. Unfortunately, the method requires the use of a third counter electrode for protecting the back side of the conductive substrate from unwanted electrochemical treatment.

There are a number of disadvantages of the methods disclosed in US patent numbers **6,346,184**, **6,110,347**, and **6,133,061**. Although the methods allow for the deposition of zinc oxide films on metallic or semiconductor conductive substrates, they require electric insulation of the rear sides of the substrates to prevent zinc oxide deposition thereon. Further, the above methods require to continuous stirring of the electrolyte

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solution during deposition. In addition, the use of aqueous electrolyte solutions requires very careful control of the pH in a narrow range to prevent precipitation of zinc / indium hydroxide at higher pH values, and to avoid dissolution of zinc / indium hydroxide / oxide from the substrate at lower pH values. Further the methods disclosed in the above US Patents may not provide reliable techniques for in-situ control of film thickness.

Yet another disadvantage of the above patents is the use of aqueous electrolyte solutions. It is known that deposition of ZnO films from aqueous zinc salt solutions will be accompanied with the formation of hydroxide which degrades the quality of ZnO films [S. Peulon, D. Lincot, Mechanistic Study of Cathodic Electrodeposition of Zinc Oxide and Zinc Hydroxychloride Films from Oxygenated Aqueous Zinc Chloride Solutions J. Electrochem. Soc., **45** (1998), **864-874**]. High deposition temperatures (60-85°C) need to be used in aqueous baths in order to shift an equilibrium balance of a hydroxide / oxide reaction to the preferred formation of oxide [D. Chu, Y. Masuda, T. Ohji, and K. Kato, Shape-Controlled Growth of $\text{In}(\text{OH})_3/\text{In}_2\text{O}_3$ Nanostructures by Electrodeposition, Langmuir **2010**, **26**(18), **14814-14820**]. Even high temperature (65-85°C) electrodeposition of indium oxide / hydroxide from aqueous solutions of indium salts does not prevent a preferential growth of indium hydroxide nanostructures. Further, drying at 80°C for 10 hours and annealing at 300°C for 30 min is required in order to obtain indium oxide by dehydration of indium hydroxide.

SUMMARY OF THE INVENTION

In accordance with one aspect of the present invention, there is provided a method of electrochemically forming an oxide layer on a flat conductive surface. The method involves positioning a working electrode bearing the flat conductive surface in opposed parallel spaced apart relation to a flat conductive surface of a counter electrode such that the flat conductive surface of the working electrode and the flat conductive surface of the counter electrode are generally opposed and horizontally oriented and define a space therebetween. The method further involves causing a volume of organic electrolyte solution containing chemicals for forming the oxide layer on the flat conductive surface of the working electrode to flood the flat conductive surface of the

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counter electrode surface and occupy the space defined between the flat conductive surface of the working electrode and the flat conductive surface of the counter electrode such that at least the flat conductive surface of the counter electrode is in contact with the organic electrolyte solution and substantially only the flat conductive surface of the working electrode is in contact with the organic electrolyte solution. The method further involves causing an electric current to flow between substantially only the flat conductive surface of the counter electrode and substantially only the flat conductive surface of the working electrode, in the organic electrolyte solution, for a period of time and at a magnitude sufficient to cause the chemicals to form the oxide layer on the flat conductive surface of the working electrode.

The method may involve causing the volume of organic electrolyte solution to occupy the space defined between the flat counter electrode surface and the flat conductive surface of the working electrode may involve holding the working electrode such that substantially only the flat conductive surface of the working electrode is in contact with the organic electrolyte solution but the entire working electrode is not immersed in the organic electrolyte solution.

Holding may include protecting a substantial portion of a side of the working electrode, opposite the flat conductive surface of the working electrode, from contact with the electrolyte solution.

Protecting may involve holding a rear side of the working electrode against a holding surface bearing a seal operably configured to contact the rear side of the working electrode adjacent an outer perimeter edge of the rear side of the working electrode.

Holding the working electrode against the holding surface may include causing a negative pressure to occur adjacent the rear side of the working electrode so that ambient pressure presses the rear side of the working electrode against the seal.

Causing the negative pressure may involve providing a vacuum adjacent the seal.

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5 The flat conductive surface of the working electrode and the flat conductive surface of the counter electrode may be spaced apart by a distance that facilitates adhesion of the organic electrolyte solution to the flat conductive surface of the working electrode and the flat conductive surface of the counter electrode due to capillary force of the organic electrolyte solution.

10 Positioning the working electrode may involve positioning the working electrode such that the flat conductive surface of the working electrode is between about 0.1% to about 20% of a length of the working electrode, from the flat conductive surface of the counter electrode.

15 Positioning the working electrode in relation to the flat conductive surface of the counter electrode may involve holding the counter electrode in a generally horizontal orientation in a container operably configured to hold the organic electrolyte solution and holding the working electrode in the container, spaced apart from the counter electrode, such that the space is defined between the flat conductive surface of the working electrode and the flat conductive surface of the counter electrode.

20 Causing the volume of organic electrolyte solution to flood the flat conductive surface of the counter electrode may involve admitting a pre-defined volume of the organic electrolyte solution into the container.

25 Admitting the pre-defined volume of the organic electrolyte solution may involve passing the pre-defined volume through an opening in the counter electrode, the opening may be in communication with the space between the flat conductive surface of the working electrode and the flat conductive surface of the counter electrode.

30 Passing the pre-defined volume through an opening may involve pumping the predefined volume of the organic electrolyte solution from a reservoir through the opening.

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The method may involve draining the organic electrolyte solution after the oxide layer is formed to a desired thickness on the flat conductive surface of the working electrode.

5 The chemicals may involve a source of oxygen sufficient to permit the oxide layer to be formed to a desired thickness.

The source of oxygen may involve dissolved oxygen or at least one oxygen precursor.

10 The source of oxygen may involve at least one oxygen precursor and the at least one oxygen precursor may involve at least one of dissolved nitrate, nitrite, hydrogen peroxide and traces of water.

Anode reaction

15 The working electrode may be formed of a material and the oxide layer may be an oxide of the material and causing the electric current to flow may involve causing the electric current to flow in a direction such that the working electrode acts as an anode.

20 The method may involve agitating the organic electrolyte solution while the electric current is flowing.

Agitating may involve causing a flow of the organic electrolyte solution to pass through the space defined between the flat conductive surface of the working electrode and the flat conductive surface of the counter electrode.

25 The organic electrolyte solution may be protic and the chemicals may include at least one of methanol, ethanol, isopropanol, ethylene glycol, and tetrahydrofurfuryl alcohol.

30 The organic electrolyte solution may be aprotic and the chemicals may include at least one of N-methylacetamide and acetonitrile.

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The organic electrolyte solution and the working electrode and the counter electrode may be generally maintained at a constant temperature of between about **15** degrees Celsius to about **90** degrees Celsius.

5 Causing the electric current to flow may involve maintaining the electric current at a level at least sufficient to maintain oxide formation on the working electrode as oxide formation occurs and presents resistance to the electric current.

10 The method may involve terminating the flow of electric current when the flow of electric current meets a criterion.

The criterion may include a condition that the oxide layer has a pre-defined thickness,

15 The current may have a current density of between about **1mA/cm²** to about **100mA/cm²**.

Cathode reaction

20 The oxide layer may be a metal oxide layer and causing the electric current to flow may involve causing the electric current to flow in a direction such that the working electrode acts as a cathode and the organic electrolyte solution may include at least one ionic source of metal.

25 The method may involve determining the pre-defined volume based on the desired thickness of the metal oxide desired to be plated onto the flat conductive surface of the cathode and based on a concentration of the ionic source of metal and a volume of the organic electrolyte solution.

30 The oxide layer may include a metal oxide film of aluminum oxide and the ionic source of metal may include at least one dissolved aluminum salt or at least one aluminate or a combination of the at least one dissolved aluminum salt or at least one aluminate.

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The oxide layer may include a metal oxide film of indium oxide and the ionic source of metal may include at least one dissolved indium salt.

5 The oxide layer may include a metal oxide film of zinc oxide and the ionic source of metal may involve at least one dissolved zinc salt or at least one zincate or a combination of the at least one dissolved zinc salt or at least one zincate.

10 The oxide layer may include a metal oxide film of aluminum-doped zinc oxide and the ionic source of metal may involve at least one dissolved zinc salt and at least one dissolved aluminum salt.

15 The oxide layer may include a metal oxide film of indium-doped zinc oxide and the ionic source of metal may involve at least one dissolved zinc salt and at least one dissolved indium salt.

The oxide layer may include a metal oxide film comprising chlorine-doped zinc oxide and the ionic source of metal may involve at least one dissolved zinc salt and the organic electrolyte solution may involve at least one dissolved chloride.

20 The oxide layer may include a metal oxide film of tin-doped indium oxide and the ionic source of metal may involve at least one dissolved indium salt and at least one dissolved tin salt.

25 The method may involve maintaining the organic electrolyte solution still while the electric current is flowing.

The organic electrolyte solution may be protic and the chemicals may include at least one of methanol, ethanol, propanol, isopropanol, ethylene glycol, and glycerol.

30 The organic electrolyte solution may be aprotic and the chemicals may include at least one of dimethylsulfoxide (DMSO) and propylene carbonate.

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The organic electrolyte solution and the working electrode and the counter electrode may be maintained at a temperature between about **15** degrees Celsius to about **90** degrees Celsius.

- 5 The method may involve terminating the flow of electric current when a pre-defined number of coulombs has passed through the organic electrolyte solution.

10 The pre-defined number of coulombs may be sufficient to cause substantially all of the ionic source of metal in the electrolyte solution to be depleted from the organic electrolyte solution and oxidized on the flat conductive surface of the working electrode to facilitate producing the oxide layer to a desired thickness.

15 Maintaining the electric current at a level may involve maintaining the electric current at a level that produces a current density of between about **0.1mA/cm²** to about **100mA/cm²** in the organic electrolyte solution.

20 The electric current may be maintained at a level that produces an electric current concentration between about **1mA/cm³** to about **1000mA/cm³** in the organic electrolyte solution.

25 The method may involve draining the organic electrolyte solution substantially depleted of the metal ions after the flat conductive surface of the cathode has been plated by the metal oxide to the desired thickness.

25 Anodic Reaction Applied to Semiconductor wafers

30 The working electrode may be a semiconductor wafer, the flat conductive surface may be on a front side or a back side of the semiconductor wafer and the oxide layer may be a semiconductor oxide layer. The semiconductor oxide may layer may be formed directly on the flat conductive surface of the working electrode or may be formed through a metal oxide layer already formed thereon.

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The semiconductor wafer may include an n-type crystalline semiconductor wafer or a p-type crystalline semiconductor wafer.

5 The flat conductive surface may be on an n-type portion or a p-type portion of the crystalline semiconductor wafer or the flat conductive surface may be on a metal oxide layer on an n-type portion or a p-type portion of the crystalline semiconductor wafer.

10 The method may further include exposing the flat conductive surface of the working electrode to light for at least a portion of a time during which the electric current may be flowing.

Exposing the flat conductive surface of the working electrode to light may involve admitting light into the space between the flat conductive surface of the working electrode and the flat conductive surface of the counter electrode.

15 Admitting light into the space may involve admitting light through openings in the counter electrode or admitting light through at least a portion of at least one peripheral edge of the space.

20 Cathodic Reaction Applied to Semiconductor Wafers

The working electrode may be a semiconductor wafer, the flat conductive surface of the working electrode may be on a front side or a back side of the semiconductor wafer and oxide may be a metal oxide. The metal oxide may be formed directly on the flat conductive surface or may be formed on a semiconductor oxide layer already on the flat conductive surface.

25 The flat conductive surface of the working electrode semiconductor wafer may involve an n-type portion or a p-type portion of a crystalline silicon photovoltaic cell.

30 The method may further include exposing the flat conductive surface of the working electrode to light for at least a portion of a time during which the electric current is flowing.

Exposing the flat conductive surface of the working electrode to light may involve admitting light into the space between the flat conductive surface of the working electrode and the flat conductive surface of the counter electrode.

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Admitting light in the space may involve admitting light through openings in the counter electrode or admitting light through at least a portion of at least one peripheral edge of the space.

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In accordance with another aspect of the present invention, there is provided an apparatus for electrochemically forming an oxide layer on a flat conductive surface. The apparatus includes a container operably configured to hold a volume of organic electrolyte solution containing chemicals for forming the oxide layer, and a counter electrode having a flat conductive surface in a generally horizontal orientation in the container such that the organic electrolyte solution floods the flat conductive surface of the counter electrode. The apparatus further includes a working electrode holder for holding a working electrode bearing the flat conductive surface onto which the oxide layer is to be formed in a generally horizontal orientation opposite, parallel and spaced apart from the counter electrode such that a space is defined between the flat conductive surface of the counter electrode and the flat conductive surface of the working electrode. At least some of the organic electrolyte solution can occupy the space and contact the flat conductive surface of the counter electrode and the flat conductive surface of the working electrode. The apparatus further includes a direct current source operably configured to be connected to the counter electrode and the working electrode to cause an electric current to flow between the counter electrode and the working electrode to cause the working electrode to act as an anode or as a cathode in the at least some of the organic electrolyte solution.

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The working electrode holder may be operably configured to hold the working electrode such that substantially only the flat conductive surface of the working electrode is in contact with the organic electrolyte solution but the entire working electrode is not immersed in the organic electrolyte solution.

The working electrode holder may include a protector operably configured to protect a substantial portion of a side of the working electrode from contact with the electrolyte solution.

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The protector may include a holding surface bearing a seal operably configured to contact a rear side of the working electrode adjacent an outer perimeter edge of the rear side of the working electrode.

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The working electrode holder may include provisions for causing a negative pressure to occur adjacent the rear side of the working electrode so that ambient pressure presses the rear side of the working electrode against the seal with sufficient force to prevent leakage of the electrolyte solution past the seal.

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The provisions for causing a negative pressure may include a vacuum opening adjacent the seal.

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The working electrode holder may be operably configured to space the flat conductive surface of the working electrode from the flat conductive surface of the counter electrode by a distance that facilitates adhesion of the organic electrolyte solution to the flat conductive surface of the working electrode and the flat conductive surface of the counter electrode due to capillary force of the organic electrolyte solution.

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The working electrode holder may be operably configured to position the working electrode such that the flat conductive surface of the working electrode is between about **0.1%** to about **20%** of a length of the working electrode, from the flat conductive surface of the counter electrode.

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The counter electrode may include a graphite plate, gas carbon plate, or graphite fabric, or a platinum plate.

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The apparatus may include provisions for admitting a pre-defined volume of the organic electrolyte solution into the container.

5 The provisions for admitting the pre-defined volume of the organic electrolyte solution may include an opening in the counter electrode, through which the pre-defined volume is passed into the container.

10 The provisions for admitting the pre-defined volume of the organic electrolyte solution may include a pump operably configured to pump the predefined volume of the organic electrolyte solution from a reservoir and through the opening.

15 The apparatus may include a drain operably configured to drain the organic electrolyte after the oxide layer is formed to a desired thickness on the flat conductive surface of the working electrode.

The chemicals may include a source of oxygen sufficient to permit the oxide layer to be formed to a desired thickness.

20 The source of oxygen may include dissolved oxygen or at least one oxygen precursor.

The source of oxygen may include at least one oxygen precursor and the at least one oxygen precursor may include at least one of dissolved nitrate, nitrite, hydrogen peroxide and traces of water.

25 Anode reaction

The direct current source may be operably configured to cause the electric current to flow in a direction in which the working electrode acts as an anode.

30 The apparatus may include provisions for agitating the electrolyte while the electric current is flowing.

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The provisions for agitating may include provisions for causing flow of the volume of electrolyte solution to pass through the space defined between the flat conductive surface of the working electrode and the flat conductive surface of the counter electrode.

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The organic electrolyte solution may be protic and the chemicals may include at least one of methanol, ethanol, isopropanol, ethylene glycol, and tetrahydrofurfuryl alcohol.

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The organic electrolyte solution may be aprotic and the chemicals may include at least one of N-methylacetamide and acetonitrile.

The apparatus may include provisions for maintaining the organic electrolyte solution, the working electrode and the counter electrode at a constant temperature of between about **15** degrees Celsius to about **90** degrees Celsius.

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The direct current source may include provisions for maintaining the electric current at a level at least sufficient to maintain oxide formation as oxide formation occurs and presents resistance to the electric current.

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The apparatus may include provisions for terminating the flow of electric current when the flow of electric current meets a criterion.

The criterion may include a condition that the oxide layer has a pre-defined thickness,

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The direct current source may include provisions for maintaining the electric current at a level to cause a current density of between about **1mA/cm²** to about **100mA/cm²** in the volume of organic electrolyte solution.

Cathode reaction

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The oxide layer may be a metal oxide layer, the electrolyte solution may include at least one ionic source of metal and the direct current source may be operably

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configured to cause the electric current to flow in a direction in which the working electrode acts as a cathode.

5 The pre-defined volume of the electrolyte solution may be sufficient to ensure the flat conductive surface of the counter electrode and the flat conductive surface of the working electrode will be in contact with the electrolyte solution. The pre-defined volume may have a concentration of metal ions sufficient to plate the metal oxide onto the flat conductive surface of the working electrode to a desired thickness of the metal oxide layer.

10 The metal oxide layer may include aluminum oxide and the ionic source of metal may include at least one dissolved aluminum salt or at least one aluminate or a combination of the at least one dissolved aluminum salt or at least one aluminate.

15 The metal oxide layer may include indium oxide and the ionic source of metal may include at least one dissolved indium salt.

20 The metal oxide layer may include zinc oxide and the ionic source of metal may include at least one dissolved zinc salt or at least one zincate or a combination of the at least one dissolved zinc salt or at least one zincate.

25 The metal oxide layer may include aluminum-doped zinc oxide and the ionic source of metal may include at least one dissolved zinc salt and at least one dissolved aluminum salt.

The metal oxide layer may include indium-doped zinc oxide and the ionic source of metal may include at least one dissolved zinc salt and at least one dissolved indium salt.

30 The metal oxide layer may include chlorine-doped zinc oxide and the ionic source of metal includes at least one dissolved zinc salt and the organic electrolyte solution may include at least one dissolved chloride.

The metal oxide layer may include tin-doped indium oxide and the ionic source of metal may include at least one dissolved indium salt and at least one dissolved tin salt.

- 5 The organic electrolyte solution may be maintained still while the electric current is flowing.

The organic electrolyte solution may be protic and the chemicals may include at least one of methanol, ethanol, propanol, isopropanol, ethylene glycol, and glycerol.

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The organic electrolyte solution may be aprotic and the chemicals may include at least one of dimethylsulfoxide (DMSO) and propylene carbonate.

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The apparatus may include provisions for maintaining the organic electrolyte solution, the working electrode and the counter electrode at a temperature between about **15** degrees Celsius to about **90** degrees Celsius.

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The apparatus may include provisions for terminating the flow of electric current when a pre-defined number of coulombs has passed through the organic electrolyte solution.

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The pre-defined number of coulombs may be sufficient to cause substantially all of the ionic source of metal in the organic electrolyte solution to be depleted from the organic electrolyte solution and oxidized on the flat conductive surface of the working electrode to facilitate producing the oxide layer to a desired thickness.

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The provisions for maintaining the electric current at a level may include provisions for maintaining the electric current at a level that produces a current density of between about **0.1mA/cm²** to about **100mA/cm²** in the organic electrolyte solution.

The provisions for maintaining the electric current may include provisions for maintaining the electric current at a level that produces an electric current

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concentration in the organic electrolyte solution between about **100mA/cm³** to about **1000mA/cm³**.

5 The apparatus may include provisions for draining the organic electrolyte solution substantially depleted of the metal ions after the flat conductive surface of the cathode has been plated by the metal oxide to the desired thickness.

Anodic Reaction Applied to Semiconductor wafers

10 The working electrode may include a semiconductor wafer, the flat conductive surface may be on a front side or a back side of the semiconductor wafer and the oxide layer may be a semiconductor oxide layer. The semiconductor oxide layer may be formed directly on the flat conductive surface of the working electrode or may be formed through a metal oxide layer already formed thereon.

15 The semiconductor wafer may include an n-type crystalline semiconductor wafer or a p-type crystalline semiconductor wafer.

20 The flat conductive surface may be on an n-type portion or a p-type portion of the crystalline semiconductor wafer or the flat conductive surface may be on a metal oxide layer on an n-type portion or a p-type portion of the crystalline semiconductor wafer.

25 The apparatus may further include provisions for exposing the flat conductive surface of the working electrode to light for at least a portion of a time during which the electric current is flowing.

The provisions for exposing the flat conductive surface of the working electrode to light may include provisions for admitting light into the space between the flat conductive surface of the working electrode and the flat conductive surface of the counter electrode.

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The provisions for admitting light into the space may include light transmissive portions in the counter electrode to permit light to pass through the light transmissive portions and impinge upon the flat conductive surface of the working electrode.

- 5 The provisions for admitting light may include a light-transmissive portion formed in the container for admitting light into the space through at least a portion of at least one peripheral edge of the space.

Cathodic Reaction Applied to Semiconductor Wafers

- 10 The working electrode may be a semiconductor wafer, the flat conductive surface of the working electrode may be on a front side or a back side of the semiconductor wafer and the oxide may be a metal oxide. The metal oxide may be formed directly on the flat conductive surface or may be formed on a semiconductor oxide layer already on the flat conductive surface. The flat conductive surface of the working electrode may
15 be on a semiconductor oxide layer on a front side or rear side of the semiconductor wafer.

The flat conductive surface of the working electrode semiconductor wafer may include an n-type portion or a p-type portion of a crystalline silicon photovoltaic cell.

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The apparatus may further include provisions for exposing the flat conductive surface of the working electrode to light for at least a portion of a time during which the electric current is flowing.

- 25 The provisions for exposing the flat conductive surface of the working electrode to light may include provisions for admitting light into the space between the flat conductive surface of the working electrode and the flat conductive surface of the counter electrode.

- 30 The provisions for admitting light into the space may include light transmissive portions in the counter electrode to permit light to pass through the light transmissive portions and impinge upon the flat conductive surface of the working electrode.

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The provisions for admitting light may include a light-transmissive portion formed in the container for admitting light into the space through at least a portion of at least one peripheral edge of the space.

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Other aspects and features of the present invention will become apparent to those ordinarily skilled in the art upon review of the following description of specific embodiments of the invention in conjunction with the accompanying figures.

10 BRIEF DESCRIPTION OF THE DRAWINGS

In drawings which illustrate embodiments of the invention,

Figure 1 is a simplified oblique view of an apparatus for forming an oxide layer on a flat conductive surface, according to a first embodiment of the invention;

15 Figure 2 is a cross sectional view of a portion of the apparatus shown in Figure 1 with a holder shown in a position in which oxide formation is operable to occur;

Figure 3 is a top plan view of a container portion of the apparatus shown in Figure 1;

Figure 4 is a bottom oblique view of the container portion shown in Figure 2;

20 Figure 5 is a top simplified oblique view of a working electrode holder of the apparatus shown in Figure 1;

Figure 6 is a bottom view of the working electrode holder shown in Figure 4;

Figure 7 is a simplified cross sectional view of the working electrode holder shown in Figure 4 holding a plate having a flat conductive surface on which an oxide layer is to be formed;

25 Figure 8 is a cross sectional view of a portion of the apparatus shown in Figure 1 with a holder shown in an alternate position in which an oxide layer can be formed;

30 Figure 9 is a simplified cross sectional view of a portion of an apparatus according to a second embodiment for forming an oxide layer onto a p-type semiconductor surface;

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Figure 10 is a simplified cross sectional view of a portion of an apparatus according to a third embodiment, for forming an oxide layer onto a p-type semiconductor surface.

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DETAILED DESCRIPTION

Referring to Figure 1, an apparatus for forming an oxide layer on a flat conductive surface is shown generally at 10. Referring to Figures 1 and 2, the apparatus 10, includes a container 12 operably configured to hold a volume 14 of organic electrolyte solution containing chemicals for forming the oxide layer. The apparatus further includes a counter electrode 16 having a flat conductive surface 18 in a generally horizontal orientation in the container 12 such that the volume 14 of organic electrolyte solution floods the flat conductive surface 18 of the counter electrode 16.

The apparatus 10 further includes a working electrode holder 20 for holding a working electrode 22 bearing a flat conductive surface 24 onto which the oxide layer is to be formed. Referring to Figure 2, the working electrode holder 20 holds the working electrode 22 in a generally horizontal orientation opposite, parallel and spaced apart from the counter electrode 16. A space 26 is thus defined between the flat conductive surface 18 of the counter electrode 16 and the flat conductive surface 24 of the working electrode 22. At least some of the volume 14 of organic electrolyte solution occupies the space 26 and is provided in sufficient quantity to simultaneously contact the flat conductive surface 18 of the counter electrode 16 and the flat conductive surface 24 of the working electrode 22.

Referring back to Figure 1, the apparatus 10 further includes a direct current source 30 operably configured to be connected to the counter electrode 16 and the working electrode 22 to cause an electric current to flow between the counter electrode and the working electrode to cause the working electrode to selectively act as an anode or as a cathode in contact with the volume of organic electrolyte solution. A polarity of the

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direct current source **30** determines whether the working electrode **22** acts as an anode or as a cathode.

5 The working electrode **22** may be made of any conductive material capable of reacting with oxygen to form an oxide on the flat conductive surface **24** thereof. An oxide of the material of the working electrode **22** may be referred to as a simple oxide. If the working electrode **22** were an iron plate, for example the simple oxide would be an iron oxide. If the working electrode **22** were a crystalline semiconductor wafer, the simple oxide would be a silicon oxide. A simple oxide can be formed by causing the polarity of
10 the working electrode **22** to be at a positive potential relative to the counter electrode **16**.

Similarly, a metal oxide can be formed on the flat conductive surface **24** of the working electrode **22** by causing the polarity of the direct current source **30** to be set such that
15 the working electrode has a negative polarity relative to the counter electrode **16**.
*Different organic electrolyte solutions are used depending on whether a simple oxide or a metal oxide is to be formed on the flat conductive surface **24**.*

In the embodiment described the working electrode **22** is a semiconductor wafer, and
20 the apparatus is used to form a semiconductor oxide on the flat conductive surface **24** of the semiconductor material itself or under a metal oxide layer already formed on the semiconductor material, by causing the polarity of the direct current source **30** to be such that the working electrode **22** has a positive potential relative to the counter electrode **16**. Alternatively, a metal oxide layer can be formed on the flat conductive
25 surface **24** of the working electrode **22** or on a semiconductor oxide layer already formed on the flat conductive surface of the working electrode, by causing the polarity of the direct current source **30** to be set such that the counter electrode **16** has a positive potential relative to the working electrode **22**. Different organic electrolyte solutions are used depending on whether a semiconductor oxide or a metal oxide is to
30 be formed on the flat conductive surface **24**

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Referring to Figure 2, regardless of whether a simple oxide layer is to be formed or a metal oxide layer is to be formed, the volume 14 of electrolyte solution includes chemicals 32 that facilitate an electrolytic reaction and the chemicals include a source of oxygen 34. Where a metal oxide layer is to be formed, the chemicals include a source of oxygen and further include an ionic source of metal 36.

Referring back to Figure 1, the apparatus 10 is described in more detail. In the embodiment shown, the container 12 is formed as a top portion of a table 40. The container 12 is generally rectangular in shape and has a bottom portion 42 and a perimeter upstanding wall 44 extending upwardly from a perimeter of the bottom portion 42. The bottom portion 42 and the perimeter upstanding wall 44 are formed of a chemically resistant material such as Teflon, polycarbonate, polystyrene or glass, for example.

The bottom portion 42 is formed with a rectangular recess 46 for receiving and holding the counter electrode 16. The counter electrode 16 is formed of a carbon graphite plate or glass graphite plate or graphite fabric material or a platinum plate, for example and has a flat conductive surface 18. The recess 46 is formed in the bottom portion 42 such that the flat conductive surface 18 of the counter electrode 16 is generally coplanar with the bottom portion 42 which, in the embodiment shown, is generally horizontally oriented.

Referring to Figure 3, the counter electrode 16 is connected to a connector 90 by a conductor 92 to facilitate easy electrical connection to the counter electrode 16.

Referring back to Figure 1, the connector 90 is connected by a wire 94 to a corresponding connector 96 of the direct current source 30. The working electrode 22 is similarly connected to the direct current source 30. Thus, the working electrode 22, the volume 14 of electrolyte solution and the counter electrode 16 form a series circuit with the current source 30. Thus, the direct current source 30 provides a direct current (DC) supply and includes an automatic control circuit 31 that can selectively adjust the polarity of an electric potential applied across the counter electrode 16 and the working electrode 22 and which can adjust the potential to increase, decrease or maintain an

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amount of electric current passing through the series circuit including the working electrode **22**, the volume **14** of electrolyte solution and the counter electrode **16**. In addition, the automatic control circuit **31** can determine whether or not a certain criterion is met such as whether or not the resistance of the series circuit has reached
5 a level at which a pre-defined current flows in the series circuit, at which time the automatic control circuit **31** selectively shuts off the current source.

Dispensing system

The counter electrode **16** has a centrally disposed opening **48** and the bottom portion
10 **42** of the container **12** has an aligned opening (not shown) aligned with the centrally disposed opening **48**, operable to admit the volume **14** of organic electrolyte solution into the container **12**.

The volume **14** of electrolyte solution is provided by a dispensing system shown
15 generally at **60**. In the embodiment shown the dispensing system **60** comprises a first reservoir **62** operably configured to hold a flushing solution **64**, and a first pump **66** for pumping a first volume of the flushing solution from the first reservoir into feed conduit **68** coupled by a flexible feed conduit **70** to the opening **48**.

20 The dispensing system **60** further includes a second reservoir **72** operably configured to hold a first electrolyte solution **74** and a second pump **76** for pumping a pre-defined volume of the first electrolyte solution **74** from the second reservoir **72** into the feed conduit **68** and through the opening **48**.

25 The dispensing system **60** further includes a third reservoir **78** operably configured to hold a second electrolyte solution **80** and a third pump **81** for pumping a pre-defined volume of the second electrolyte solution **80** from the third reservoir **78** into the feed conduit **68** and through the opening **48**.

30 A controller **82** is provided to selectively operate the first, second or third pump (**66**, **76**, **81**) to selectively pump the flushing solution **64** or a pre-defined volume of the first or second electrolyte solutions (**74**, **80**) into the feed conduit **50** and through the opening

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48, to flood the flat conductive surface **18** of the counter electrode **16** so it can be used as part of an electrolytic cell with the working electrode **22** in the container **12**.

The flushing solution **64** may include an organic solvent or water, for example.

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The first and second electrolyte solutions **74**, **80** are configured to facilitate use of the working electrode **22** as either an anode or a cathode, respectively, to suit the type of oxide layer to be formed. Each of the first and second electrolyte solutions **74**, **80** includes chemicals including a source of oxygen sufficient to permit the oxide layer to be formed to a desired thickness. The source of oxygen may include dissolved oxygen or at least one oxygen precursor such as at least one of dissolved nitrate, nitrite, hydrogen peroxide and traces of water. The concentration of dissolved oxygen precursor ready for use in the electrochemical process of forming the oxide layer should be selected such that at least enough source oxygen is provided in the volume of electrolyte dispensed into the container **12** to facilitate formation of an oxide layer of a desired thickness.

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The controller **82** selectively causes a first pre-defined volume of the first electrolyte solution **74** to be admitted into the container **12** and to cause the current source **30** to be configured to cause the working electrode **22** to act as an anode. The first pre-defined volume must be sufficient to ensure the flat conductive surface **18** of the counter electrode **16** and the flat conductive surface **24** of the working electrode **22** are in contact with the first pre-defined volume of the first electrolyte solution **74**. With the working electrode **22** acting as an anode, the oxide formed on the flat conductive surface **24** of the working electrode **22** will be an oxide of the material of which the working electrode is made, i.e. a simple oxide. Thus, for example, if the working electrode **22** is a crystalline silicon semiconductor wafer, a silicon oxide layer can be formed on the flat conductive surface thereof, or under a metal oxide layer already formed thereon, when the first electrolyte solution **74** is used and the current source **30** causes the working electrode **22** to have a positive potential relative to the counter electrode **16**.

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Where the working electrode **22** is used as an anode, the organic electrolyte solution may be protic and the chemicals in the first electrolyte solution **74** may include at least one of methanol, ethanol, isopropanol, ethylene glycol, and tetrahydrofurfuryl alcohol. Alternatively, the first electrolyte solution **74** may be a protic and the chemicals may include at least one of N-methylacetamide and acetonitrile.

Similarly, the controller **82** may alternatively operate the third pump **81** to cause a second pre-defined volume of the second electrolyte solution **80** to be admitted into the container **12** and to cause the current source **30** to be configured to cause the working electrode **22** to act as a cathode. The second pre-defined volume of the second electrolyte solution **80**, must be sufficient to ensure the flat conductive surface **18** of the counter electrode **16** and the flat conductive surface **24** of the working electrode **22** are in contact with the second pre-defined volume of the second electrolyte solution **80**.

In this embodiment where the working electrode **22** is a crystalline silicon semiconductor wafer, a metal oxide layer will be formed on the flat conductive surface **24** thereof or on a semiconductor oxide layer already formed on the flat conductive surface thereof, when the second electrolyte solution **80** is used and the current source **30** causes the working electrode **22** to have a negative potential relative to the counter electrode **16**.

The second electrolyte solution **80** may be protic and the chemicals may include at least one of methanol, ethanol, propanol, isopropanol, ethylene glycol, and glycerol. Alternatively, the second electrolyte solution **80** may be aprotic and the chemicals may include at least one of dimethylsulfoxide (DMSO) and propylene carbonate.

Also, the second electrolyte solution **80** includes at least one ionic source of metal to facilitate the formation of a metal oxide layer on the flat conductive surface **24** of the working electrode **22** or on a simple oxide layer already formed on the flat conductive surface **24**. The amount of ionic source of metal in the second pre-defined volume must be sufficient to facilitate formation of the metal oxide layer on the flat conductive surface **24** of the working electrode **22** to a desired thickness.

Where an aluminum oxide layer is intended to be formed on a PV cell, for example, the ionic source of metal may include at least one dissolved aluminum salt or at least one aluminate or a combination of the at least one dissolved aluminum salt or at least one aluminate. The dissolved aluminium salt may be selected from nitrate, chloride, or sulphate for example. The organic electrolyte solution may contain from **0.0001Eq/L** (gram equivalent/litre) to **0.1 Eq/L** of aluminum or from **0.0001Eq/L** of aluminum to concentration of saturated solution to produce an aluminum oxide film having a thickness of about **10nm** to about **200nm** on a photovoltaic (PV) cell **4in – 8in (10.16cm – 20.32cm)** square.

Where an indium oxide layer is to be formed on a PV cell the ionic source of metal may include at least one dissolved indium salt. The at least one dissolved indium salt may be selected from nitrate, chloride, or sulphate for example. The organic electrolyte solution may contain from **0.0001Eq/L** (gram equivalent/litre) to **0.1 Eq/L** of indium or from **0.0001Eq/L** of indium to concentration of saturated solution to produce an indium oxide film having a thickness of about **50nm** to about **130nm** on a PV cell **4in – 8in (10.16cm – 20.32cm)** square.

Where a zinc oxide layer is to be formed on a PV cell, the ionic source of metal may include at least one dissolved zinc salt or at least one zincate or a combination of the at least one dissolved zinc salt or at least one zincate. The at least one dissolved zinc salt may be selected from nitrate, chloride, or sulphate for example. The organic electrolyte solution may contain from **0.0001Eq/L** (gram equivalent/litre) to **0.1 Eq/L** of zinc or from **0.0001Eq/L** of zinc to concentration of saturated solution to produce a zinc oxide film having a thickness of about **50nm** to about **130nm** on a PV cell **4in – 8in (10.16cm – 20.32cm)** square.

Where an aluminum-doped zinc oxide layer is to be formed on a PV cell, the ionic source of metal may include at least one dissolved zinc salt and at least one dissolved aluminum salt. The dissolved zinc salt may be selected from nitrate, chloride, or sulphate for example. The dissolved aluminum salt may be selected from nitrate,

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chloride, or sulphate for example. The organic electrolyte solution may contain gram equivalents of zinc and aluminum in the ratio of between about **500/1** to **3:1** to produce an aluminium-doped zinc oxide film having a thickness of about **80nm** to about **100nm** on a PV cell **4in – 8in (10.16cm – 20.32cm)**square.

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Where an indium-doped zinc oxide layer is to be formed on a PV cell, the ionic source of metal may include at least one dissolved zinc salt and at least one dissolved indium salt. The dissolved zinc salt may be selected from nitrate, chloride, or sulphate for example, and the at least one dissolved indium salt, may be selected from nitrate, chloride, or sulphate for example. The organic electrolyte solution may contain gram equivalents of zinc and indium in the ratio of between about **200/1** to **5:1** to produce an indium-doped zinc oxide film having a thickness of about **50nm** to about **130nm** on a PV cell **4in – 8in (10.16cm – 20.32cm)**square.

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Where a chlorine-doped zinc oxide layer is to be formed on a PV cell, the ionic source of metal may include at least one dissolved zinc salt and at least one dissolved chloride. The at least one zinc salt may be selected from nitrate, chloride, or sulphate for example. The organic electrolyte solution may contain from **0.0001Eq/L** (gram equivalent/litre) to **0.1 Eq/L** of zinc or from **0.0001Eq/L** of zinc to concentration of saturated solution and from **0.001 Eq/L** to **0.1 Eq/L** of chloride or from **0.001 Eq/L** of chloride to concentration of saturated solution to produce a chlorine-doped zinc oxide film having a thickness of about **50nm** to about **130nm** on a PV cell **4in – 8in (10.16cm – 20.32cm)** square.

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Where a tin-doped indium oxide layer is to be formed on a PV cell, the ionic source of metal may include at least one dissolved indium salt and at least one dissolved tin salt. The dissolved indium salt may be selected from nitrate, chloride, or sulphate for example, and the at least one dissolved tin salt may be selected from nitrate, chloride, or sulphate for example. The organic electrolyte solution may contain gram equivalents of indium and tin in the ratio of between about **200/1** to **1:1** to produce a tin-doped indium oxide film having a thickness of about **50nm** to about **130nm** on a PV cell **4in – 8in (10.16cm – 20.32cm)**square.

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The controller **82** and the direct current source **30** are in communication with each other to ensure that the first pre-defined volume of the first electrolyte solution **74** is admitted into the container **12** prior to causing an electric current to flow in a direction in which the working electrode **22** acts as an anode and to ensure that the second pre-defined volume of the second electrolyte solution **80** is admitted into the container **12** prior to causing an electric current to flow in a direction in which the working electrode **22** acts as a cathode, and to ensure that the container **12** is flushed with flushing solution **64** prior to and between successive uses and so that with each successive use a new predefined volume of either the first or second electrolyte solutions **74** or **80** is admitted into the container **12**, without contamination from a previous use.

Referring back to Figure **3**, to facilitate flushing the container of spent electrolyte solution, the bottom portion **42** of the container **12** has drainage channels **100** extending along perimeter margins of the bottom portion, adjacent the counter electrode **16**. The drainage channels **100** are in communication with a drain opening **102**. The drainage channels **100** are suitably graded to direct liquid (i.e. the flushing solution **64**, or the first or second electrolyte solutions **74** or **80** respectively) into the drain opening **102**.

Referring to Figure **4**, a solenoid valve **104** is attached to the underside of the container **12** and is in communication with the drain opening **102** and with a drain conduit **106**. The solenoid valve **104** is controlled by the controller (**82** in Figure **1**) to be selectively opened and closed to drain flushing solution **64** or any first or second electrolyte solution (**74**, **80**) from the container **12** or to contain flushing solution or the first or second electrolyte solution (**74**, **80**) in the container **12**, as desired. Thus, the solenoid valve **104** is kept closed when admitting the first or second electrolyte solution (**74**, **80**) into the container **12** and during an electrolytic operation and is opened to drain spent electrolyte solution from the container **12** after an electrolytic operation and/or for flushing when flushing solution **64** is admitted into the container **12**. The controller **82** drainage channels **100**, drain opening **102**, and solenoid valve **104** cooperate to drain electrolyte solution from the container **12** to a designated collector, after an

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electroplating cycle has been completed. Separate collectors may be provided to collect respective volumes of flushing solution **64**, first electrolyte solution **74** and second electrolyte solution and a suitable valving system may be provided to selectively direct liquid received in the drain opening **102** to the appropriate collector.

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Referring back to Figure **1**, the table **40** includes a support **110** that extends upwardly from the container **12**. To the support **110** is connected a slidable collar **112** operable to slide on the support and relative to the support in a vertical direction indicated by arrow **114**. A stop **116** may be securely fastened to the support **110** and may serve to limit the movement of the slidable collar **112** in the vertical direction. The slidable collar **112** is connected to a chuck mount **118** to which is fastened a working electrode holder **120**. The mount **118** allows for movement of the working electrode holder **120** in the direction of arrow **122** generally in a direction perpendicular to the direction of movement of the slidable collar **162** indicated by arrow **114**. The mount **118** has a clamp **124** for holding the working electrode holder **120** and which provides for vertical adjustment of the working electrode holder relative to the mount **118**. Of course, robotics can alternatively be used to position the working electrode holder **120** in the locations described herein.

Referring to Figure **5** in this embodiment, the apparatus includes provisions for maintaining the electrolyte solution, the working electrode **22** and the counter electrode **16** at a temperature between about **15** degrees Celsius to about **90** degrees Celsius with an accuracy of about +/- **1** degree Celsius. These provisions include forming the working electrode holder **120** to include a conductive plate **130** which, in this embodiment, includes a metal plate of aluminium having a thickness of approximately **2cm**, but the plate could alternatively be made of stainless steel, silver or platinum or other metals or metal alloys, for example and it could have a different thickness. The plate **130** is formed to have a plurality of passages **132** sealed by plugs **134** and in communication with first and second tubing connectors **136** and **138** on a top surface **164** of the metal plate **130**.

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Referring back to Figure 1, source and drain tubes **140** and **142** are connected to the first and second tubing connectors **136** and **138** respectively. The drain tube **142** is in communication with a liquid heater **144** and a pump **146** is in communication with the heater through a pump conduit **148**. Operation of the pump **146** causes the pump to draw thermal liquid from the heater **91** through the pump conduit **148** and cause it to pass through the source tube **140** to the first tubing connector **136** and then through the passages **132** and out the second tubing connector **138** into the drain tube **142** and back to the liquid heater **144**. The arrangement of the passages **132** and the tubing connectors **86** and **88** permits thermal fluid such as water to be pumped from the first tubing connector **86**, through the passages **132** to the second tubing connector **88**, for example, to provide for a flow of thermal fluid to be passed through the plate **80** to keep the working electrode **22** it holds at a generally constant temperature. The thermal fluid may be water or a 50/50 mixture of water and ethylene glycol antifreeze, for example. Other thermal fluids compatible with the metal used to form the plate **130** may alternatively be used. Or alternatively the plate **130** may be heated electrically.

Referring back to Figure 5, the working electrode holder **120** has an upstanding member **150** fastened to the plate **130** by an electrically insulating mount **152**, which electrically isolates the upstanding member **150** from the plate **130**. Referring to Figure 1, the upstanding member **150** is held by the clamp **124** to mount the working electrode holder **120** thereto.

Referring to Figure 6, an underside surface **160** of the plate **130** is shown. The plate has a bore **162** extending therethrough, between a top surface **164** of the plate as shown in Figure 5 and the underside surface **160** of the plate as shown in Figure 6. The underside surface **160** has a vacuum supply channel **166** cut therein (such as by a milling machine, for example) in communication with the bore **162** and in communication with a perimeter channel **168** extending around a perimeter margin of the underside surface **160**. Referring to Figures 5 and 6, the bore **162** is in communication with a vacuum hose connector **170** which, referring to Figure 1, is connected to a vacuum hose **172** connected to a vacuum pump **174** mounted on the table **40**.

Referring to Figures 1 and 6, when the vacuum pump 174 is activated a vacuum is applied to the bore 162 and is communicated to the channels 166 and 168, particularly when a working electrode 22 is placed in the immediate vicinity of the underside surface 160.

Referring to Figure 5, in the embodiment shown, the vacuum hose connector 170 is metallic and the plate 130 is metallic. The vacuum hose connector 170 has screw threads for connecting it to the plate 130 and since both the vacuum hose connector and the plate are metallic they are in electrical contact with each other. A ring 171 of an electrical terminal lug 173 is received on the screw threads of the vacuum hose connector 170 before screwing the vacuum hose connector into the bore 162 in the plate 130. Referring to Figures 1 and 5, a wire 175 connected to the electrical terminal lug 173 is electrically connected to a second terminal 177 of the direct current source 30. Use of the metallic plate 130 and the metallic vacuum hose connector 170 facilitates an easy electrical connection of the wire 175 to the plate 130. Of course, any other suitable method of connecting a wire to the plate could be used.

Referring to Figure 6, the underside surface 160 also has a perimeter groove 181 which holds a rubber seal 182 formed of a soft rubber material such as silicone rubber, for example. An area 184 bounded by the perimeter groove 181 is intended to be the same shape as, but slightly smaller than the working electrode 22 to be held by the working electrode holder 120. The perimeter groove 181 is formed and the rubber seal 182 is sized to have a width between about 1mm to 3mm and a thickness between about 0.1 mm to about 1mm such that the rubber seal protrudes no more than between about 0.1mm to about 0.5mm from the underside surface 160 of the plate 130, as seen best in Figure 7. All surfaces of the plate 130, except the area 184 bounded by the perimeter groove and the rubber seal 182 are deeply-pre-anodized to protect these surfaces. This anodization forms an electrically insulative layer and causes these surfaces to be chemically inert to the first and second electrolyte solutions 74 and 78 and to the flushing solution 64. Alternatively, these surfaces can be pre-coated with an inert coating such as Teflon®, for example. Therefore, as explained below, the plate

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130 is not involved in the electrochemical reactions that occur when the working electrode **22** and counter electrode **16** are placed in contact with the first or second electrolyte solutions **74** or **80** and current is conducted therethrough. The area **184** is not pre-anodized and remains conductive to facilitate electrical connection of the working electrode **22** to the plate **130**.

Alternatively, a brass plate can be substituted for the aluminum plate **130**. The surfaces of the brass plate that are exposed to the electrolyte may be coated with Teflon® or other coating chemically inert to the first and second electrolyte solutions **74**, **80** and the flushing solution **64**. Where a brass plate is used, the area **184** bounded by the perimeter groove **181** may be plated with silver, for example to provide for good electrical contact with the working electrode **22**. The use of the brass plate may be best suited for a production version of the apparatus.

Operation

Referring to Figures **1** and **7**, to use the apparatus **10**, an object on which an oxide layer is to be formed, is brought into the vicinity of the underside surface **160** of the plate **130** and then the vacuum pump **174** is activated. The object is intended to be generally flat planar in shape and in this embodiment is a semiconductor wafer or photovoltaic cell. In other embodiments other conductive or semiconductive planar objects may similarly act as the object. The term "conductive" as used herein in connection with the object onto which an oxide layer is to be formed is meant to include conductive and semiconductive materials.

The object has a back side surface **180** and bears the flat planar conductive surface **24** onto which the oxide layer will be formed, on a side of the object opposite the back side surface **180**. The back side surface **180** is drawn into contact with the underside surface **160** of the plate **130** by the vacuum communicated to the channels **168** (and **166** shown in Figure **6**) through the bore **162**. The vacuum communicated to the channels **166** and **168** creates a negative pressure between the back side surface **180** and the plate **130** such that the back side surface **180** is held pressed against the

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underside surface **160** of the plate **130** by ambient air pressure. The object should be suitably dimensioned and carefully positioned relative to the underside surface **160** prior to actuating the vacuum pump (**174**) such that the rubber seal **182** will contact the back side surface **180** closely adjacent an outer edge of the object, as shown in Figure 7, such that most of the back side surface **180** is within the area **184** bounded by the rubber seal **182**. The ambient air pressure presses the object tightly against the rubber seal **182** effectively sealing off the area **184** of the back side surface **180** bounded by the rubber seal **182**. Thus, the rubber seal **182** will act to protect the area **184** of the back side surface **180** bounded by the rubber seal from contact with the electrolyte when the apparatus is in use.

Since the rubber seal **182** protrudes from the underside surface **160** by only a very small amount, and since the seal extends closely adjacent the perimeter edge of the object the object is held in a relatively flat planar condition, although a central interior portion **183** of the object will experience more vacuum because it is near the bore **162**. The central interior portion **183** will flex and will be drawn into mechanical and electrical contact with the underside surface **160** of the plate **130**. Since the plate **130** is in electrical contact with the second terminal **177** of the direct current source, when the object is in electrical contact with the underside surface **160** of the plate **130**, it is also in electrical contact with the direct current source **30** through the wire **175** connected to the vacuum hose connector **170**. With the object secured to and in electrical contact with the working electrode holder **120**, the object becomes the working electrode **22**.

Referring to Figures **1** and **2**, with the working electrode **22** in place, the slidable collar **112** is slid down the support **110** until the flat conductive surface **24** of the working electrode **22** and the flat conductive surface **18** of the counter electrode **16** are parallel and spaced apart and define the space **26** therebetween. The counter electrode **16** and working electrode **22** are horizontally oriented, as are the flat conductive surface **18** of the counter electrode and the flat conductive surface **24** of the working electrode. In this embodiment, the working electrode **22** is positioned such that the flat conductive surface **24** of the working electrode is a distance **190** away from the flat conductive

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surface **18** of the counter electrode **16**. The distance **190** may be between about **0.1%** to about **20%** of a length **192** of the working electrode **22**, for example.

Where the working electrode **22** is a semiconductor wafer or photovoltaic cell for example, it may have the shape of a square rectangular plate having a side length of **15** cm, for example and thus the distance **190** may be pre-defined to be between about **0.15** mm to about **30** mm, for example. Desirably, the clamp **124** and slideable collar **112** are designed to provide for adjustment of the separation between the flat conductive surface **24** of the working electrode **22** and the flat conductive surface **18** of the counter electrode **16** within a range of about **0.15** mm to about **30**mm, to suit the size of the working electrode **22**. The clamp **124** may be pre-set such that when the slidable collar **112** is resting on the stop **116**, the pre-defined distance **190** is provided between the flat conductive surface **24** of the working electrode **22** and the flat conductive surface **18** of the counter electrode **16**.

With the working electrode **22** positioned in close, parallel spaced apart relation as shown in Figure **2**, the controller **82** shown in Figure **1** operates the first or second pump **76** or **81** to dispense a pre-defined volume of first or second electrolyte solution **74** or **80** into the space **26** between the flat conductive surface **18** of the counter electrode **16** and the flat conductive surface **24** of the working electrode **22** such that the flat conductive surface **18** is submerged in the electrolyte solution and substantially only the flat conductive surface **24** of the working electrode **22** is in contact with the electrolyte solution. The working electrode **22** is not entirely immersed in the organic electrolyte solution because the rubber seal **182** prevents the organic electrolyte solution from contacting the back side surface **180** of the working electrode **22**. Furthermore, in the embodiment shown, because the flat conductive surface **18** of the counter electrode **16** and the flat conductive surface **24** of the working electrode **22** are so closely spaced apart, adhesion of the electrolyte to the flat conductive surface of the working electrode and the flat conductive surface of the counter electrode occurs due to capillary force of the electrolyte. Therefore, in this embodiment, only a small amount of electrolyte solution is required to facilitate the electrolytic reaction that will occur when current is passed through the electrolyte.

Alternatively, as shown in Figure 8, a greater spacing may be employed between the flat conductive surface **24** of the working electrode **22** and the flat conductive surface **18** of the counter electrode **16**, but in this embodiment, the capillary force of the electrolyte solution (**74** or **80**) does not maintain the electrolyte in the space between the flat conductive surface of the working electrode and the flat conductive surface of the counter electrode. This embodiment uses relatively more electrolyte solution (**74** or **80**). To keep the volume of electrolyte solution (**74** or **80**) used to a minimum, it may be desirable to make an inside surface **194** of the perimeter upstanding wall **44** just slightly larger than the working electrode **22**. For example, the perimeter upstanding wall may be formed such that a distance **196** or spacing, between any edge **198** of the working electrode **22** and an inside surface **194** of an adjacent portion of the perimeter upstanding wall **44** may be between about **8mm** to about **10mm** or at least enough to accommodate the width of a drainage channel **100** between the edge **198** of the working electrode **22** and the inside surface **194** of an adjacent portion of the perimeter upstanding wall **44**. Alternatively, the perimeter upstanding wall **44** can be undercut to provide space for drainage channels immediately adjacent to edge **198** of the working electrode **22** while occupying a space immediately above the drainage channels to keep the volume of electrolyte required to a minimum.

With the working electrode **22** positioned in the container **12** as shown in Figure 7 or 8, the container is first flushed with flushing solution **64** to remove any contaminants. To do this, the controller **82** actuates the solenoid valve **104** to open it to facilitate draining and actuates the first pump **66** to pump a continuous stream of flushing solution through the opening **48** into the space **26** between the working electrode **22** and the counter electrode **16**.

After flushing, the container **12** is ready to receive a volume of electrolyte solution. The specific electrolyte solution to be received in the container **12** is selected depending on whether a simple oxide layer comprising an oxide of the material of which the working electrode is made is intended to be formed on the conductive surface **24** or whether a metal oxide layer is intended to be formed on the conductive surface. Where the

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working electrode is a semiconductor wafer of PV cell and where a simple oxide layer is to be formed, the conductive surface **24** of the material forming the working electrode may be virgin or may already have a metallic oxide formed thereon. Where the working electrode is a semiconductor wafer or PV cell and where a metallic oxide layer is to be formed, the conductive surface **24** of the material forming the working electrode may be virgin or may already have a simple oxide layer formed thereon.

Use of the Working Electrode as an Anode

Where the working electrode is a semiconductor wafer of PV cell and it is desired to form a simple oxide layer on a virgin conductive surface of the working electrode **22** or under a metal oxide layer already formed on the virgin conductive surface, the controller **82** actuates the second pump **76** to cause it to pump a first pre-defined volume of the first electrolyte solution **74** into the feed conduit **68**, through the flexible feed conduit **70** and through the opening **48** formed in the counter electrode **16** such that the first pre-defined volume is admitted into the container **12** and some of the first pre-defined volume is in the space **26** and contained between the flat conductive surface **18** of the counter electrode **16** and the flat conductive surface **24** of the working electrode **22** and is in electrical contact therewith.

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Where the spacing between the counter electrode **16** and the working electrode **22** is as shown in Figure **2**, the first pre-defined volume will be less than if the spacing were as shown in Figure **8**. Therefore the first electrolyte solution **74** will have to be configured to have a concentration of dissolved oxygen precursor suitable for use with the selected embodiment such that the first predefined volume will have enough dissolved oxygen to facilitate growth of the oxide layer at least to the desired thickness.

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The back side surface **180** of the working electrode **22** is protected from exposure to the first electrolyte solution **74** by the seal **182** and thus virtually only the flat conductive surface **24** of the working electrode is exposed to the first electrolyte solution **74** and will participate in the electrolytic reaction. Since the surfaces of the plate **130** exposed

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to the electrolyte are pre-anodized or pre-coated with chemically resistant material the material of the plate does not participate in the electrolytic reaction.

5 With the flat conductive surface **24** of the working electrode **24** and the flat conductive surface **18** of the counter electrode **16** in contact with the first electrolyte solution **74**, the controller **82** actuates the current source **30** such that the working electrode **22** is at a positive (+) potential relative to the counter electrode **16** which is at a negative (-) potential relative to the working electrode. This causes an electric current to flow through the first pre-defined volume of the first electrolyte solution **74** between the
10 working electrode **22** and the counter electrode **16** and provides for electrochemical decomposition of the oxygen precursor. For example, if the oxygen precursor is water, the water is broken down into ions of hydrogen H^+ and oxygen O^{2-} . The oxygen ions migrate to the flat conductive surface **24** of the working electrode **22** and the surface oxidizes, thereby forming an oxide on the surface. At the same time the hydrogen ions
15 migrate to the flat conductive surface **18** of the counter electrode **16**, where they are reduced to form hydrogen gas H_2 .

The depth of semiconductor oxide formation in the flat conductive surface **24** can be increased with increased potential between the working electrode and the counter
20 electrode and with increased time and vice-versa and thus can be controlled by the automatic control circuit **31**.

In the embodiment shown, the automatic control circuit **31** maintains the electric current at a level at least sufficient to maintain oxide formation as oxide formation
25 occurs and presents increasing resistance to the electric current. For example, the automatic control circuit **31** may increase the potential between the working electrode **22** and the counter electrode **16** to maintain the current at a given level as the resistance presented by the forming semiconductor oxide layer increases. Or the automatic control circuit **31** may cause the current to increase or decrease as the oxide
30 layer is formed. Knowing the voltage applied and the current being maintained the increasing resistance presented by the forming oxide layer is monitored by the automatic controller circuit **31** until a target resistance associated with a semiconductor

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oxide layer of a target thickness is reached at which time the automatic control circuit **31** shuts off the current source **30**. Thus, in effect the automatic control circuit **31** terminates the flow of electric current when the current meets a criterion. In the embodiment described, the criterion is that the current must be impressed through a resistance of a target value indicative of a semiconductor oxide layer of a target thickness, for example.

Alternatively, the criterion may include a time measurement, wherein the criterion is met when the electric current has been applied at a defined level for a target amount of time indicative of development of a semiconductor oxide layer of a target thickness.

The automatic control circuit **31** may be configured to maintain the electric current at a level to cause a current density of between about $1\text{mA}/\text{cm}^2$ to about $100\text{mA}/\text{cm}^2$ in the first pre-defined volume of electrolyte solution **74**, for example.

During formation of the semiconductor oxide layer on the working electrode **22**, it is desirable to agitate the first pre-defined volume of the first electrolyte solution **74** while the electric current is flowing. Agitation may be provided by causing a flow in the first pre-defined volume of electrolyte solution **74** such that the electrolyte solution is not stagnant or still. This may be effected through the use of a vibrator on the table **40** to transfer vibratory movement to the counter electrode **16** and ultimately to the first pre-defined volume of electrolyte solution **74** in contact therewith such that a flow of the first pre-defined volume of electrolyte solution **74** passes through the space **26** defined between the flat conductive surface **24** of the working electrode **22** and the flat conductive surface **18** of the counter electrode **16**. Alternatively, the container **12** may be configured with a circulation pump (not shown) to circulate the first pre-defined volume of electrolyte solution **74** through the space **26** defined between the flat conductive surface **24** of the working electrode **22** and the flat conductive surface **18** of the counter electrode **16**.

As indicated earlier, desirably, the electrolyte solution **74**, **80**, working electrode **22** and the counter electrode **16** are maintained at a constant temperature of between about

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15 degrees Celsius to about **90** degrees Celsius by maintaining the thermal fluid in the heater **144** at a temperature within this range and operating the pump **146** to pump the thermal fluid through the plate **130** of the working electrode holder **120**.

5 Under the above conditions, a semiconductor oxide layer is formed on the flat conductive surface **24** of the working electrode **22**. Once the semiconductor oxide layer has reached the desired thickness, the current source **30** is shut off and the controller **82** actuates the solenoid valve **104** and then actuates the first pump **66** to dispense a volume of flushing solution **64** through the bore **162** and into the container
10 **12**. Sustained dispensing of the flushing solution **64** flushes the spent first pre-defined volume of the first electrolyte solution **74** from the container **12** and into a catchment apparatus for recycling or at least de-toxification.

After a period of flushing, the working electrode **22** may then be raised out of the
15 container **12** by the working electrode holder **120** and passed to separate material handling apparatus (not shown) for further processing such as annealing, for example. Alternatively, the separate material handling apparatus may simply turn the working electrode **22** upside down and start the above described process again, where the surface on which the semiconductor oxide layer was just formed becomes the back
20 side surface **180** secured by the vacuum to the working electrode holder **120** and the side that was formerly the back side surface **180** is ready for a cycle of electrolytic action as described to form a semiconductor oxide layer on what was formerly the back side surface **180** of the working electrode.

25 Alternatively, the flat conductive surface that was just anodized by the process described above may be subjected to formation of a metal oxide layer as described below, on the semiconductor oxide layer just formed or the back side surface may be subjected to formation of a metal oxide layer as described below.

30 Cathode reaction

Where it is desired to form a metal oxide layer on a virgin conductive surface of the working electrode **22** or on a semiconductor oxide layer already formed on the virgin

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conductive surface, the controller **82** actuates the third pump **81** to cause it to pump a second pre-defined volume of the second electrolyte solution **80** into the feed conduit **68**, through the flexible feed conduit **70** and through the opening **48** formed in the counter electrode **16** such that the second pre-defined volume is admitted into the container **12** such that some of second pre-defined volume is in the space **26** and is contained between the flat conductive surface **18** of the counter electrode **16** and the flat conductive surface **24** of the working electrode **22** and is in electrical contact therewith.

Where the spacing between the counter electrode **16** and the working electrode **22** is as shown in Figure **2**, the second pre-defined volume will be less than if the spacing were as shown in Figure **8**. Therefore the second electrolyte solution **80** will have to be configured to have a concentration of dissolved oxygen precursor suitable for use with the selected embodiment such that the second predefined volume will have enough dissolved oxygen precursor to facilitate growth of the metal oxide layer to the desired thickness.

In addition, the concentration of the source of metal in the second pre-defined volume of electrolyte solution **80** is selected such that when substantially all of the metal ions of the source of metal are depleted from the second pre-defined volume of electrolyte solution **80**, the metal oxide formed on the surface of the flat conductive surface **24** of the working electrode **130** is of a thickness corresponding to the amount of the source of metal in the volume of electrolyte solution admitted into the container **12**. Thus, to produce a suitable second electrolyte solution it will be necessary to determine how many moles of dissolved metal ions will be needed to form the metal oxide layer to have a target thickness and to ensure that at least this amount of dissolved metal ions are present in the second-predefined volume of second electrolyte solution **80**.

The back side surface **180** of the working electrode **22** is protected from exposure to the second electrolyte solution **80** by the seal **182** and thus virtually only the flat conductive surface **24** of the working electrode is exposed to the second electrolyte solution **80** and will participate in the electrolytic reaction.

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With the flat conductive surface **24** of the working electrode **22** and the flat conductive surface **18** of the counter electrode **16** in contact with the second electrolyte solution **80**, the controller **82** actuates the current source **30** such that the working electrode **22** is at a negative (-) potential relative to the counter electrode **16** which is at a positive (+) potential relative to the working electrode **22**. This causes an electric current to flow through the second pre-defined volume of the second electrolyte solution **80** between the working electrode **22** and the counter electrode **16** and provides a source of electrons for reduction of the dissolved oxygen or oxygen precursors and for interaction with metal ions dissolved in the solution in the vicinity of the conductive surface **24** of the working electrode **22**. This results in precipitation of metal oxide directly onto the conductive surface **24** of the working electrode **22**.

The rate of growth of metal oxide can be increased and decreased with increased or decreased current density in the second electrolyte solution **80** and thus can be controlled by the automatic control circuit **31**. The rate of growth of metal oxide can also be controlled by the temperature of the second electrolyte solution **80**.

As the number of metal ions in the second electrolyte precipitate as metal oxide on the flat conductive surface **24**, the thickness of the metal oxide layer on the flat conductive surface increases and the second electrolyte solution becomes depleted of metal ions. When the second electrolyte solution is substantially depleted of metal ions, the metal oxide layer will have a particular thickness. To ensure substantially all of the metal ions have been depleted from the second electrolyte solution, it is necessary to provide a sufficient number of coulombs by way of the electric current. A coulomb meter may be used to measure the number of coulombs that have passed through the electrolyte or a time integral of the electrical current may be calculated to give the number of coulombs. Calibration curves plotting oxide layer thickness vs. coulombs or time at specified electric currents, metal ion concentrations and at different temperatures and for different surfaces, such as p-type or n-type crystalline semiconductor surfaces may be produced before production runs and used to determine suitable metal ion

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concentrations, temperatures, electric current and time parameters for production runs to produce metal oxide layers of desired thickness.

In the embodiment shown, the automatic control circuit **31** maintains the electric current at a level at least sufficient to maintain metal oxide formation as metal oxide layer formation occurs. The forming metal oxide layer may present resistance to the electric current. The automatic control circuit **31** may increase the potential between the working electrode **22** and the counter electrode **16** to maintain the current at a given level as the resistance presented by the forming metal oxide layer increases. Or, the automatic control circuit **31** may cause the current to increase or decrease as the metal oxide layer is formed. Regardless of whether the current is increased or decreased or maintained constant, the automatic control circuit **31** terminates the flow of electric current when a pre-defined number of coulombs has passed through the second electrolyte solution **80**, the pre-defined number being sufficient to ensure that substantially all of the ionic source of metal in the second electrolyte solution has been depleted from the second electrolyte solution and oxidized on the flat conductive surface of the working electrode **22** to form the metal oxide layer to a desired thickness. In the embodiment described, the time integral of current is indicative of a pre-defined number of coulombs of electrons having passed through the second electrolyte solution **80**, the pre-defined number of coulombs being indicative of a target thickness of the metal oxide layer.

The automatic control circuit **31** may control the electric current to produce a current density in the second pre-defined volume of second electrolyte solution on the order of about **0.1 mA/cm²** to about **100 mA/cm²**. The optimum current density is selected in a range corresponding to preferable deposition of a specific metal oxide and elimination of a potential competitive reaction of metal deposition. For example, a suitable current density for deposition of aluminum oxide may be in a range of between about **1mA/cm²** to about **5mA/cm²**.

In the embodiment shown in Figure **2**, high current concentrations in the range of about **1mA/cm³** to about **1000mA/cm³** and preferably in the range of about **10mA/cm³** to

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about 100mA/cm^3 are possible due to the small separation distance **190** between the flat conductive surface **24** of the working electrode **22** and the flat conductive surface **18** of the counter electrode **16**.

5 During formation of the metal oxide layer on the working electrode **22**, it is desirable not to agitate the second pre-defined volume of the second electrolyte solution **80** while the electric current is flowing and to maintain the second pre-defined volume of the second electrolyte solution still.

10 As indicated earlier, desirably, the second pre-defined volume of the second electrolyte solution **80**, the working electrode **22** and the counter electrode **16** are maintained at a constant temperature of between about **15** degrees Celsius to about **90** degrees Celsius by maintaining the thermal fluid in the heater **144** at a temperature within this range and operating the pump **146** to pump the thermal fluid through the plate **130** of
15 the working electrode holder **120**.

The thickness of the metal oxide layer formed on the flat conductive surface **24** is controlled by the amount of dissolved metal ions in the second electrolyte solution **80** subject to a sufficient number of coulombs of electrons passing through the second
20 electrolyte solution **80**. Thus, the number of moles of dissolved metal ions required to form the metal oxide layer to the desired thickness must first be determined and then the concentration of dissolved metal ions required in the second pre-defined volume of second electrolyte solution can be determined knowing that there must be sufficient
25 volume to ensure the flat conductive surface **24** of the working electrode **22** and the flat conductive surface **18** of the counter electrode **16** will be in contact with the second electrolyte solution. This provides for very accurate control of the thickness of the metal oxide layer and provides for near **100%** utilization of all metal ions in the second electrolyte solution **80**.

30 When a sufficient number of coulombs has passed through the second electrolyte solution **80** and substantially all of the metal ions of the source of metal in the second pre-defined volume of second electrolyte solution **80** are depleted from the second

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electrolyte solution and formed on the flat conductive surface **24** of the working electrode **22** as a metal oxide film of the desired thickness, a resistance to electric current flow is presented by the metal oxide layer and this is detected by the automatic control circuit **31**. In response the automatic control circuit **31** shuts off the current source **30**. Once the current source **30** is shut off the controller **82** actuates the solenoid valve **104** and then actuates the first pump **66** to dispense a volume of flushing solution through the opening **48** and into the container **12**. Sustained dispensing of the flushing solution flushes the spent second pre-defined volume of the second electrolyte solution from the container **12** and into a catchment apparatus for recycling or at least de-toxification.

The vacuum may then be released by switching off the vacuum pump **108** and dropping the working electrode **22**, now having a metal oxide plated surface, onto material handling equipment (not shown) for further processing stages, such as annealing, for example.

After the working electrode **22** has been removed for further processing and the depleted electrolyte has been drained from the container **12**, the apparatus **10** is then ready to receive another working electrode bearing a flat conductive surface on which a metal oxide is to be formed, or the working electrode **22** can be turned over and re-attached to the working electrode holder **120** by the surface on which the metal oxide layer was just formed and the back side surface **180** can be exposed for metal oxide layer formation according to the process above.

Using the above-described processes, a semiconductor oxide layer may be formed on a virgin semiconductor surface and a metal oxide layer may be formed on the semiconductor oxide layer. The formation of the metal oxide layer in this case should be done while the semiconductor oxide layer is still "wet" i.e. just formed and before any annealing.

Similarly, using the above processes a metal oxide layer can be formed directly on a virgin semiconductor surface and a semiconductor oxide layer may be formed after the

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metal oxide layer has been formed. The formation of the semiconductor oxide layer in this case should be done while the metal oxide layer is still "wet".

5 It has been found that the semiconductor oxide layer penetrates the flat conductive surface and grows into that surface as the semiconductor oxide layer is formed. This occurs whether the semiconductor oxide layer is formed on a virgin surface of the semiconductor material or after a metal oxide layer has already been formed by the process described above, on the virgin surface.

10 It is also desirable to form the desired semiconductor oxide layer and metal oxide layer on the front and/or back surfaces before any annealing. Annealing is ultimately necessary to create the necessary crystal structure in the semiconductor oxide or metallic oxide resulting from the above process.

15 Depending on the chemical composition and thickness of the semiconductor oxide or plated metal oxide, annealing may be performed at temperatures in the range of about **300** degrees celcius to about **700** degrees celcius in an air atmosphere or in a special gas atmosphere. A special gas atmosphere for this purpose may include a gas comprised of about **3%** to about **10%** hydrogen balanced with nitrogen or inert gas, for
20 example. The annealing process may take about **15min** to about **2** hours, for example.

The above apparatus is particularly well suited for forming metal oxides on semiconductor devices such as photovoltaic cells. In this case, the flat conductive surface **24** of the working electrode **22** is a surface of an n-type or p-type
25 semiconductor substrate and the apparatus **10** is form a simple oxide film or a metal oxide film on the surface of the n-type or p-type semiconductor substrate. Such films may be used to passivate and to improve the optical qualities of the semiconductor substrate surface.

30 In one experiment, an aluminum oxide film was plated onto a p-type Si crystalline wafer using the process described above. The second electrolyte was a saturated solution of AlCl_3 in isopropanol. The electrolyte was held at a temperature of about **30** degrees

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Celsius and the current density was about $0.25\text{mA}/\text{cm}^2$ for 2min. X-ray diffraction analysis (not shown) revealed a transition aluminum oxide in the form $k\text{-Al}_2\text{O}_3$ with typical peaks at $2\theta_1 = 32.903$ degrees (more intensive) and $2\theta_2 = 32.092$ (less intensive). The surface area of the working electrode **22** was 100cm^2 . The distance
5 **190** between the flat conductive surface **24** of the working electrode **22** and the flat conductive surface **18** of the counter electrode **16** was 1mm. The concentration of Aluminum ions was 0.005Eq/L (gram equivalent/liter).

Referring to Figure **9**, where the working electrode **22** is a p-type semiconductor
10 substrate and the direct current source causes current to flow such that the working electrode acts as a cathode, resulting in metal oxide plating on the flat conductive surface **24** or where the working electrode **22** is an n-type semiconductor substrate and the direct current source causes electric current to flow such that the working electrode
15 functions as an anode resulting in the formation of a semiconductor oxide layer on the flat conductive surface, the oxide forming process can be enhanced by illuminating or admitting light onto the flat conductive surface **24** of the working electrode **22** while the electric current is flowing. To do this, the distance **190** between the flat conductive surface **24** of the working electrode **22** and the flat conductive surface **18** of the counter
20 electrode **16** may be set to approximately 3cm, for example and the volume of first or second electrolyte solution **74**, **80** is increased to ensure that the flat conductive surface **24** and the flat conductive surface **18** are still in contact with the electrolyte solution. To achieve this, the perimeter upstanding wall **44** of the container **12** is increased in height and is provided with a light transparent window **220** formed of a
25 glass of polystyrene, for example, for admitting light **222** produced by an external light source (not shown) to pass through the window **220**, through the electrolyte solution **74**, **80**, and onto the flat conductive surface **24** of the working electrode **22**.

Referring to Figure **10**, in another embodiment the distance **190** may be decreased by providing openings such as shown at **230** in the counter electrode **16** and by causing
30 the bottom portion **42** of the container **12** to be formed of a transparent material such as a glass of polystyrene, for example. A light source **232** may be placed beneath the container **12** such that light can pass through the bottom portion **42** of the container and

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through the openings **230** of the counter electrode **16** and through the volume of electrolyte solution to reach the flat conductive surface **24** of the working electrode **22**.

5 The above apparatus and method provide for precision control over the distance between the flat conductive surface **24** of the working electrode **22** and the flat conductive surface **18** of the counter electrode **16**, the amount of the electrolyte solution, and the amount of dissolved metal salts and other chemical components in the electrolyte solution. This enables precision control of the thickness of the semiconductor oxide or metal oxide formed on the surface of the object, which has
10 particular advantages when the object is a semiconductor substrate for a PV cell, for example. In addition, since the distance between the flat conductive surface **24** of the working electrode **22** and the flat conductive surface **18** of the counter electrode **16** is relatively small, the resistance presented by the electrolyte solution is relatively small, which enables the use of low voltage while achieving high current densities which
15 results in very low heat generation within the electrolyte solution producing only small convective movement within the electrolyte, which is particularly advantageous when forming metal oxides on the surface of semiconductors such as crystalline silicon wafers used for photovoltaic cells.

20 In addition, the above apparatus and methods avoid the use of separate electric insulation on the back side of the working electrode due to the sealing effect of the rubber seal on the working electrode holder, and the above method and apparatus provide for nearly **100%** utilization of the metal ions in the volume of second electrolyte used in a given plating operation. Finally, the above apparatus and method allow the
25 same apparatus to be selectively used for the formation of semiconductor oxides and metal oxides on the same conductive surface of a semiconductor wafer or a PV cell with only a change in electrolyte and a change in current direction.

30 While specific embodiments of the invention have been described and illustrated, such embodiments should be considered illustrative of the invention only and not as limiting the invention as construed in accordance with the accompanying claims.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

- 5 1. A method of electrochemically forming an oxide layer on a flat conductive surface, the method comprising:

0 positioning a working electrode bearing the flat conductive surface in opposed parallel spaced apart relation to a flat conductive surface of a counter electrode such that said flat conductive surface of said working electrode and said flat conductive surface of said counter electrode are generally opposed, horizontally oriented, and define a space therebetween;

5 causing a volume of organic electrolyte solution containing chemicals for forming said oxide layer on said flat conductive surface of said working electrode to flood said flat conductive surface of said counter electrode surface and occupy the space defined between said flat conductive surface of said working electrode and said flat conductive surface of said counter electrode such that at least said flat conductive surface of said counter electrode is in contact with said organic electrolyte solution and substantially only the flat conductive surface of the working electrode is in contact with the organic electrolyte solution; and

5 causing an electric current to flow between substantially only the flat conductive surface of said counter electrode and substantially only the flat conductive surface of the working electrode, in the organic electrolyte solution, for a period of time and at a magnitude sufficient to cause said chemicals to form said oxide layer on said flat conductive surface of said working electrode.

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2. The method of claim 1 wherein causing said volume of organic electrolyte solution to occupy the space defined between said flat counter electrode surface and said flat conductive surface of said working electrode comprises holding the working electrode such that substantially only the flat conductive surface of the working electrode is in contact with the organic electrolyte solution but the entire working electrode is not immersed in the organic electrolyte solution.
3. The method of claim 2 wherein holding comprises protecting a substantial portion of a side of said working electrode, opposite said flat conductive surface of said working electrode, from contact with said organic electrolyte solution.
4. The method of claim 3 wherein protecting comprises holding a rear side of said working electrode against a holding surface bearing a seal operably configured to contact said rear side of said working electrode adjacent an outer perimeter edge of said rear side of said working electrode.
5. The method of claim 4 wherein holding said working electrode against said holding surface comprises causing a negative pressure to occur adjacent said rear side of said working electrode so that ambient pressure presses said rear side of said working electrode against said seal.
6. The method of claim 5 wherein causing said negative pressure comprises providing a vacuum adjacent said seal.
7. The method of any one of claims 1-6 wherein said flat conductive surface of said working electrode and said flat conductive surface of said counter electrode are spaced apart by a distance that facilitates adhesion of the organic electrolyte solution to the flat conductive surface of said working electrode and said flat conductive surface of said counter electrode due to capillary force of the organic electrolyte solution.

8. The method of any one of claims **1-7** wherein positioning said working electrode comprises positioning said working electrode such that said flat conductive surface of said working electrode is between about **0.1%** to about **20%** of a length of said working electrode, from said flat conductive surface of said counter electrode.
9. The method of any one of claims **1-8** wherein positioning said working electrode in relation to said flat conductive surface of said counter electrode comprises holding said counter electrode in a generally horizontal orientation in a container operably configured to hold said organic electrolyte solution and holding said working electrode in said container and spaced apart from said counter electrode such that said space is defined between said flat conductive surface of said working electrode and said flat conductive surface of said counter electrode.
10. The method of claim **9** wherein causing said volume of organic electrolyte solution to flood said flat conductive surface of said counter electrode comprises admitting a pre-defined volume of said organic electrolyte solution into said container.
11. The method of claim **10** wherein admitting the pre-defined volume of said organic electrolyte solution comprises passing said pre-defined volume through an opening in the counter electrode, the opening being in communication with the space between said flat conductive surface of said working electrode and said flat conductive surface of said counter electrode.
12. The method of claim **11** wherein passing said pre-defined volume through an opening comprises pumping said predefined volume of said organic electrolyte solution from a reservoir through said opening.

13. The method of any one of claims **1-12** further comprising draining the organic electrolyte solution after said oxide layer is formed to a desired thickness on said flat conductive surface of said working electrode.
- 5 14. The method of any one of claims **1-13** wherein said chemicals comprise a source of oxygen sufficient to permit said oxide layer to be formed to a desired thickness.
- 0 15. The method of claim **14** wherein said source of oxygen comprises dissolved oxygen or at least one oxygen precursor.
16. The method of claim **15** wherein said source of oxygen comprises at least one oxygen precursor and wherein the at least one oxygen precursor comprises at least one of dissolved nitrate, nitrite, hydrogen peroxide and traces of water.
- 5 17. The method of any one of claims **14-16** wherein the working electrode is formed of a material and wherein the oxide layer is an oxide of said material and wherein causing said electric current to flow comprises causing said electric current to flow in a direction such that said working electrode acts as an anode.
- 10 18. The method of any one of claims **1-17** further comprising agitating said organic electrolyte solution while said electric current is flowing.
19. The method of claim **18** wherein agitating comprises causing a flow of said organic electrolyte solution to pass through the space defined between said flat conductive surface of said working electrode and said flat conductive surface of said counter electrode.
- 5 20. The method of any one of claims **17-19** wherein said organic electrolyte solution is protic and said chemicals include at least one of methanol, ethanol, isopropanol, ethylene glycol, and tetrahydrofurfuryl alcohol.
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- 21.** The method of any one of claims **17-19** wherein said organic electrolyte solution is aprotic and said chemicals include at least one of N-methylacetamide and acetonitrile.
- 22.** The method of any one of claims **17-21** wherein said organic electrolyte solution and said working electrode and said counter electrode are generally maintained at a constant temperature of between about **15** degrees Celsius to about **90** degrees Celsius.
- 23.** The method of any one of claims **17-22** wherein causing said electric current to flow comprises maintaining said electric current at a level at least sufficient to maintain oxide formation on said working electrode as oxide formation occurs and presents resistance to said electric current.
- 24.** The method of any one of claims **17-23** further comprising terminating said flow of electric current when said flow of electric current meets a criterion.
- 25.** The method of claim **24** wherein said criterion includes a condition that said oxide layer has a pre-defined thickness,
- 26.** The method of any one of claims **17-25** wherein said current has a current density of between about 1mA/cm^2 to about 100mA/cm^2 in the organic electrolyte solution.
- 27.** The method of any one of claims **1-16** wherein the oxide layer is a metal oxide layer and wherein causing said electric current to flow comprises causing said electric current to flow in a direction such that said working electrode acts as a cathode and wherein said organic electrolyte solution includes at least one ionic source of metal.
- 28.** The method of claim **27** further comprising determining said pre-defined volume based on the desired thickness of the metal oxide desired to be plated onto said

flat conductive surface of said cathode and based on a concentration of said ionic source of metal and a volume of said organic electrolyte solution.

- 5 **29.** The method of claim **27** wherein said oxide layer includes a metal oxide film comprising aluminum oxide and wherein said ionic source of metal comprises at least one dissolved aluminum salt or at least one aluminate or a combination of said at least one dissolved aluminum salt or at least one aluminate.
- 0 **30.** The method of claim **27** wherein said oxide layer includes a metal oxide film comprising indium oxide and wherein said ionic source of metal comprises at least one dissolved indium salt.
- 15 **31.** The method of claim **27** wherein said oxide layer includes a metal oxide film comprising zinc oxide and wherein said ionic source of metal comprises at least one dissolved zinc salt or at least one zincate or a combination of said at least one dissolved zinc salt or at least one zincate.
- 20 **32.** The method of claim **27** wherein said oxide layer includes a metal oxide film comprising aluminum-doped zinc oxide and wherein said ionic source of metal comprises at least one dissolved zinc salt and at least one dissolved aluminum salt.
- 25 **33.** The method of claim **27** wherein said oxide layer includes a metal oxide film comprising indium-doped zinc oxide and wherein said ionic source of metal comprises at least one dissolved zinc salt and at least one dissolved indium salt.
- 30 **34.** The method of claim **27** wherein said oxide layer includes a metal oxide film comprising chlorine-doped zinc oxide and wherein said ionic source of metal comprises at least one dissolved zinc salt and wherein said organic electrolyte solution comprises at least one dissolved chloride.

35. The method of claim **27** wherein said oxide layer includes a metal oxide film comprising tin-doped indium oxide and wherein said ionic source of metal comprises at least one dissolved indium salt and at least one dissolved tin salt.
- 5 36. The method of any one of claims **27-35** further comprising maintaining said organic electrolyte solution still while said electric current is flowing.
- 0 37. The method of any one of claims **27-36** wherein said organic electrolyte solution is protic and wherein said chemicals include at least one of methanol, ethanol, propanol, isopropanol, ethylene glycol, and glycerol.
- 5 38. The method of any one of claims **27-36** wherein said organic electrolyte solution is aprotic and wherein said chemicals include at least one of dimethylsulfoxide (DMSO) and propylene carbonate.
39. The method of any one of claims **27-38** wherein said organic electrolyte solution and said working electrode and said counter electrode are maintained at a temperature between about **15** degrees Celsius to about **90** degrees Celsius.
- 0 40. The method of any one of claims **27-39** further comprising terminating said flow of electric current when a pre-defined number of coulombs has passed through said electrolyte solution.
- 5 41. The method of any one of claims **40** wherein said pre-defined number of coulombs is sufficient to cause substantially all of said ionic source of metal in said electrolyte solution to be depleted from said organic electrolyte solution and oxidized on said flat conductive surface of said working electrode to facilitate producing said oxide layer to a desired thickness.
- 0 42. The method of claim **41** wherein maintaining said electric current at a level comprises maintaining said electric current at a level that produces a current

density of between about 0.1mA/cm^2 to about 100mA/cm^2 in said organic electrolyte solution.

5 **43.** The method of any one of claims **27-42** wherein said electric current is maintained at a level that produces an electric current concentration between about 1mA/cm^3 to about 1000mA/cm^3 in the organic electrolyte solution.

0 **44.** The method of claim **41-43** further comprising draining the organic electrolyte solution substantially depleted of said metal ions after said flat conductive surface of said cathode has been plated by said metal oxide to said desired thickness.

15 **45.** A method of forming an oxide layer on a semiconductor wafer, the method comprising the method of any one of claims **1-26** wherein said working electrode comprises said semiconductor wafer, said flat conductive surface is on a front side or a back side of said semiconductor wafer and said oxide layer is a semiconductor oxide layer.

20 **46.** The method of claim **45** wherein said semiconductor wafer includes an n-type crystalline semiconductor wafer or a p-type crystalline semiconductor wafer.

25 **47.** The method of claim **46** wherein said flat conductive surface is on an n-type portion or a p-type portion of said crystalline semiconductor wafer or wherein said flat conductive surface is on a metal oxide layer on an n-type portion or a p-type portion of said crystalline semiconductor wafer.

30 **48.** The method of claim **46** wherein the method further includes exposing said flat conductive surface of said working electrode to light for at least a portion of a time during which said electric current is flowing.

35 **49.** The method of claim **48** wherein exposing said flat conductive surface of said working electrode to light comprises admitting light into said space between said

flat conductive surface of said working electrode and said flat conductive surface of said counter electrode.

50. The method of claim **49** wherein admitting light into said space comprises admitting light through openings in said counter electrode or admitting light through at least a portion of at least one peripheral edge of said space.
51. A method of forming a metal oxide layer on a semiconductor wafer, the method comprising the method of any one of claims **27-44** wherein said working electrode comprises said semiconductor wafer, said flat conductive surface of said working electrode is on a front side or a back side of said semiconductor wafer or wherein said flat conductive surface of said working electrode is on a semiconductor oxide layer on a front side or rear side of said semiconductor wafer.
52. The method of claim **51** wherein said flat conductive surface of said working electrode semiconductor wafer includes an n-type portion or a p-type portion of a crystalline silicon photovoltaic cell.
53. The method of claim **51** or **52** wherein the method further includes exposing the flat conductive surface of said working electrode to light for at least a portion of a time during which said electric current is flowing.
54. The method of claim **53** wherein exposing said flat conductive surface of said working electrode to light comprises admitting light into said space between said flat conductive surface of said working electrode and said flat conductive surface of said counter electrode.
55. The method of claim **54** wherein admitting light in said space comprises admitting light through openings in said counter electrode or admitting light through at least a portion of at least one peripheral edge of said space.

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- 56.** An apparatus for electrochemically forming an oxide layer on a flat conductive surface, the apparatus comprising:

a container operably configured to hold a volume of organic electrolyte solution containing chemicals for forming said oxide layer;

a counter electrode having a flat conductive surface in a generally horizontal orientation in said container such that said organic electrolyte solution floods said flat conductive surface of said counter electrode;

a working electrode holder for holding a working electrode bearing the flat conductive surface onto which said oxide layer is to be formed in a generally horizontal orientation opposite, parallel and spaced apart from said counter electrode such that a space is defined between said flat conductive surface of said counter electrode and said flat conductive surface of the working electrode, wherein at least some of said organic electrolyte solution can occupy said space and contact said flat conductive surface of said counter electrode and said flat conductive surface of the working electrode;

an direct current source operably configured to be connected to said counter electrode and the working electrode to cause an electric current to flow between said counter electrode and the working electrode to cause the working electrode to act as an anode or as a cathode in said at least some of said organic electrolyte solution.

- 57.** The apparatus of claim **56** wherein the working electrode holder is operably configured to hold the working electrode such that substantially only the flat conductive surface of the working electrode is in contact with the organic electrolyte solution but the entire working electrode is not immersed in the organic electrolyte solution.

58. The apparatus of claim **57** wherein said working electrode holder includes a protector operably configured to protect a substantial portion of a side of the working electrode from contact with the organic electrolyte solution.
- 5 59. The apparatus of claim **58** wherein said protector includes a holding surface bearing a seal operably configured to contact a rear side of the working electrode adjacent an outer perimeter edge of the rear side of the working electrode.
- 0 60. The apparatus of claim **59** wherein said working electrode holder includes means for causing a negative pressure to occur adjacent the rear side of the working electrode so that ambient pressure presses the rear side of the working electrode against the seal with sufficient force to prevent leakage of said electrolyte solution past said seal.
- 15 61. The apparatus of claim **60** wherein said means for causing a negative pressure comprises a vacuum opening adjacent said seal.
- 20 62. The apparatus of any one of claims **56-61** wherein said working electrode holder is operably configured to space said flat conductive surface of the working electrode from said flat conductive surface of said counter electrode by a distance that facilitates adhesion of the organic electrolyte solution to the flat conductive surface of the working electrode and said flat conductive surface of said counter electrode due to capillary force of the organic electrolyte solution.
- 25 63. The apparatus of any one of claims **56-62** wherein said working electrode holder is operably configured to position the working electrode such that said flat conductive surface of the working electrode is between about **0.1%** to about **20%** of a length of the working electrode, from said flat conductive surface of said counter electrode.
- 30

64. The apparatus of any one of claims **56-63** wherein said counter electrode comprises a graphite plate, gas carbon plate, or graphite fabric, or a platinum plate.
- 5 65. The apparatus of claim **64** further comprising means for admitting a pre-defined volume of said organic electrolyte solution into said container.
66. The apparatus of claim **65** wherein said means for admitting said pre-defined volume of said organic electrolyte solution comprises an opening in said counter
0 electrode, through which said pre-defined volume is passed into said container.
67. The apparatus of claim **66** wherein said means for admitting said pre-defined volume of said organic electrolyte solution comprise a pump operably configured to pump said predefined volume of said organic electrolyte solution from a
5 reservoir and through said opening.
68. The apparatus of any one of claims **56-67** further comprising a drain operably configured to drain the organic electrolyte after said oxide layer is formed to a desired thickness on the flat conductive surface of the working electrode.
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69. The apparatus of any one of claims **56-68** wherein said chemicals comprise a source of oxygen sufficient to permit said oxide layer to be formed to a desired thickness.
- 15 70. The apparatus of claim **69** wherein said source of oxygen comprises dissolved oxygen or at least one oxygen precursor.
71. The apparatus of claim **70** wherein said source of oxygen comprises at least one oxygen precursor and wherein the at least one oxygen precursor comprises
20 at least one of dissolved nitrate, nitrite, hydrogen peroxide and traces of water.

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72. The apparatus of any one of claims **56-71** wherein said direct current source is operably configured to cause said electric current to flow in a direction in which the working electrode acts as an anode.
- 5 73. The apparatus of any one of claims **56-72** further comprising means for agitating said electrolyte while said electric current is flowing.
74. The apparatus of claim **73** wherein said means for agitating comprises means for causing flow of said volume of organic electrolyte solution to pass through
0 the space defined between said flat conductive surface of the working electrode and said flat conductive surface of said counter electrode.
75. The apparatus of any one of claims **72-74** wherein said organic electrolyte solution is protic and said chemicals include at least one of methanol, ethanol,
5 isopropanol, ethylene glycol, and tetrahydrofurfuryl alcohol.
76. The apparatus of any one of claims **72-74** wherein said organic electrolyte solution is aprotic and said chemicals include at least one of N-methylacetamide and acetonitrile.
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77. The apparatus of any one of claims **72-76** further comprising means for maintaining said organic electrolyte solution, the working electrode and said counter electrode at a constant temperature of between about **15** degrees Celsius to about **90** degrees Celsius.
15
78. The apparatus of any one of claims **72-77** wherein said direct current source comprises means for maintaining said electric current at a level at least sufficient to maintain oxide formation as oxide formation occurs and presents resistance to said electric current.
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79. The apparatus of claim any one of claims **72-78** further comprising means for terminating said flow of electric current when said flow of electric current meets a criterion.

5 **80.** The apparatus of claim **79** wherein said criterion includes a condition that said oxide layer has a pre-defined thickness,

0 **81.** The apparatus of any one of claims **72-80** wherein said direct current source comprises means for maintaining said electric current at a level to cause a current density of between about $1\text{mA}/\text{cm}^2$ to about $100\text{mA}/\text{cm}^2$ in said volume of organic electrolyte solution.

5 **82.** The apparatus of any one of claims **56-71** wherein the oxide layer is a metal oxide layer, wherein said electrolyte solution includes at least one ionic source of metal and wherein said direct current source is operably configured to cause said electric current to flow in a direction in which the working electrode acts as a cathode.

10 **83.** The apparatus of claim **82** wherein said pre-defined volume of said electrolyte solution is sufficient to ensure said flat conductive surface of said counter electrode and said flat conductive surface of said working electrode will be in contact with said electrolyte solution and wherein said pre-defined volume has a concentration of metal ions sufficient to plate said metal oxide onto said flat conductive surface of said working electrode to a desired thickness of said metal oxide layer.

15 **84.** The apparatus of claim **82** wherein said metal oxide layer comprises aluminum oxide and wherein said ionic source of metal comprises at least one dissolved aluminum salt or at least one aluminate or a combination of said at least one dissolved aluminum salt or at least one aluminate.

85. The apparatus of claim **82** wherein said metal oxide layer comprises indium oxide and wherein said ionic source of metal comprises at least one dissolved indium salt.
- 5 86. The apparatus of claim **82** wherein said metal oxide layer comprises zinc oxide and wherein said ionic source of metal comprises at least one dissolved zinc salt or at least one zincate or a combination of said at least one dissolved zinc salt or at least one zincate.
- 0 87. The apparatus of claim **82** wherein said metal oxide layer comprises aluminum-doped zinc oxide and wherein said ionic source of metal comprises at least one dissolved zinc salt and at least one dissolved aluminum salt.
- 5 88. The apparatus of claim **82** wherein said metal oxide layer comprises indium-doped zinc oxide and wherein said ionic source of metal comprises at least one dissolved zinc salt and at least one dissolved indium salt.
- 0 89. The apparatus of claim **82** wherein said metal oxide layer comprises chlorine-doped zinc oxide and wherein said ionic source of metal comprises at least one dissolved zinc salt and wherein said organic electrolyte solution comprises at least one dissolved chloride.
- 5 90. The apparatus of claim **82** wherein said metal oxide layer comprises tin-doped indium oxide and wherein said ionic source of metal comprises at least one dissolved indium salt and at least one dissolved tin salt.
91. The apparatus of any one of claims **82-90** wherein said organic electrolyte solution is maintained still while said electric current is flowing.
- 0 92. The apparatus of any one of claims **82-91** wherein said organic electrolyte solution is protic and wherein said chemicals include at least one of methanol, ethanol, propanol, isopropanol, ethylene glycol, and glycerol.

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93. The apparatus of any one of claims **82-92** wherein said organic electrolyte solution is aprotic and wherein said chemicals include at least one of dimethylsulfoxide (DMSO) and propylene carbonate.
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94. The apparatus of any one of claims **82-93** further comprising means for maintaining said organic electrolyte solution, the working electrode and said counter electrode at a temperature between about **15** degrees Celsius to about **90** degrees Celsius.
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95. The apparatus of any one of claims **82-94** further comprising means for terminating said flow of electric current when a pre-defined number of coulombs has passed through said organic electrolyte solution.
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96. The apparatus of any one of claims **95** wherein said pre-defined number of coulombs is sufficient to cause substantially all of said ionic source of metal in said organic electrolyte solution to be depleted from said organic electrolyte solution and oxidized on said flat conductive surface of said working electrode to facilitate producing said oxide layer to a desired thickness.
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97. The apparatus of claim **96** wherein said means for maintaining said electric current at a level comprises means for maintaining said electric current at a level that produces a current density of between about **0.1mA/cm²** to about **100mA/cm²** in said organic electrolyte solution.
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98. The apparatus of any one of claims **82-97** wherein said means for maintaining said electric current comprises means for maintaining said electric current at a level that produces an electric current concentration in said organic electrolyte solution between about **100mA/cm³** to about **1000mA/cm³**.
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99. The apparatus of claim **82-98** further comprising means for draining the organic electrolyte solution substantially depleted of said metal ions after said flat

conductive surface of said cathode has been plated by said metal oxide to said desired thickness.

5 **100.** An apparatus for forming an oxide layer on a semiconductor wafer, the apparatus comprising the apparatus of any one of claims **56-71** wherein the working electrode comprises said semiconductor wafer, said flat conductive surface is on a front side or a back side of said semiconductor wafer and said oxide layer is a semiconductor oxide layer.

0 **101.** The apparatus of claim **100** wherein said semiconductor wafer includes an n-type crystalline semiconductor wafer or a p-type crystalline semiconductor wafer.

5 **102.** The apparatus of claim **101** wherein said flat conductive surface is on an n-type portion or a p-type portion of said crystalline semiconductor wafer or wherein said flat conductive surface is on a metal oxide layer on an n-type portion or a p-type portion of said crystalline semiconductor wafer.

10 **103.** The apparatus of claim **101** wherein the apparatus further includes means for exposing said flat conductive surface of the working electrode to light for at least a portion of a time during which said electric current is flowing.

15 **104.** The apparatus of claim **103** wherein said means for exposing said flat conductive surface of the working electrode to light comprises means for admitting light into said space between said flat conductive surface of the working electrode and said flat conductive surface of said counter electrode.

20 **105.** The apparatus of claim **104** wherein said means for admitting light into said space comprises light transmissive portions in said counter electrode to permit light to pass through said light transmissive portions and impinge upon said flat conductive surface of said working electrode.

- 106.** The apparatus of claim **104** wherein said means for admitting light comprises a light-transmissive portion formed in said container for admitting light into said space through at least a portion of at least one peripheral edge of said space.
- 5 **107.** An apparatus for forming a metal oxide layer on a semiconductor wafer, the apparatus comprising the apparatus of any one of claims **82-99** wherein the working electrode comprises said semiconductor wafer, said flat conductive surface of the working electrode is on a front side or a back side of said semiconductor wafer or wherein said flat conductive surface of the working
0 electrode is on a semiconductor oxide layer on a front side or rear side of said semiconductor wafer.
- 5 **108.** The apparatus of claim **107** wherein said flat conductive surface of said working electrode semiconductor wafer includes an n-type portion or a p-type portion of a crystalline silicon photovoltaic cell.
- 10 **109.** The apparatus of claim **107** or **108** wherein the apparatus further includes means for exposing the flat conductive surface of the working electrode to light for at least a portion of a time during which said electric current is flowing.
- 15 **110.** The apparatus of claim **109** wherein said means for exposing said flat conductive surface of the working electrode to light comprises means for admitting light into said space between said flat conductive surface of the working electrode and said flat conductive surface of said counter electrode.
- 20 **111.** The apparatus of claim **109** wherein said means for admitting light into said space comprises light transmissive portions in said counter electrode to permit light to pass through said light transmissive portions and impinge upon said flat conductive surface of said working electrode.
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- 112.** The apparatus of claim **109** wherein said means for admitting light comprises a light-transmissive portion formed in said container for admitting light into said space through at least a portion of at least one peripheral edge of said space.