APPARATUS AND METHODS FOR CHEMICAL ELECTRODEPOSITION ON A SUBSTRATE FOR SOLAR CELL FABRICATION

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ABSTRACT

The invention relates generally to electrodeposition apparatus and methods. The invention finds particular use in fabricating thin film solar cells. Electrodeposition is improved by using a continuous thin film flow of electrodeposition solution between a substrate and a counter electrode, positioned in close proximity to each other, while the plating current is applied. Apparatus for carrying out methods described herein are highlighted particularly by flow manifolds that allow electrodeposition in the manner described.
Figure 3
1200

START

FLOW ELECTROLYTE BETWEEN SUBSTRATE AND COUNTER ELECTRODE IN CLOSE PROXIMITY TO EACH OTHER USING A FLOW MANIFOLD WHICH SUPPLIES A CONTINUOUS FLOW OF ELECTROLYTE TO ONE SURFACE OF THE SUBSTRATE

APPLY PLATING POTENTIAL TO SUBSTRATE AND COUNTER ELECTRODE

END

Figure 12
APPARATUS AND METHODS FOR CHEMICAL ELECTRODEPOSITION ON A SUBSTRATE FOR SOLAR CELL FABRICATION

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of priority under 35 U.S.C. §119 to U.S. Provisional Application Ser. No. 61/169,211, filed Apr. 14, 2009, and to U.S. Provisional Application Ser. No. 61/171,007, filed Apr. 20, 2009, both of which are incorporated by reference herein for all purposes.

FIELD OF INVENTION

This invention relates generally to electrodeposition apparatus and methods. Methods and apparatus of the invention find particular use in solar cell fabrication.

BACKGROUND

Electrodeposition is a plating process that uses electrical current to reduce or oxidize chemical species of a desired material from a solution and coat a conductive substrate with a thin layer of that material. An electroplating apparatus typically includes two electrodes, a substrate serving as one electrode and a counter electrode. Additionally, a reference electrode may also be employed. In an electrodeposition process, typically the part to be coated is one of the electrodes and the coating material is supplied from the electrolyte in which the electrodes are immersed. In electroplating, the electrolyte is replenished periodically with the chemical species being deposited on the substrate. Sometimes, the electrode that is not being coated can be a source of the chemical species in order to replenish the electrolytic solution.

Solar or photovoltaic cells are devices that convert photons into electricity by the photovoltaic effect. Solar cells are assembled together to make solar panels, solar modules, or photovoltaic arrays. Solar cells are stacked structures, having layers of materials, including photovoltaic materials, stacked on a substrate for support of the stack. There are many fabrication techniques used fabricating the individual layers of the stack. One particularly useful method is electrodeposition, however there are drawbacks to conventional apparatus and methods in this respect.

SUMMARY

The invention relates generally to electrodeposition apparatus and methods. The invention finds particular use in fabricating thin film solar cells. The inventors have found that electrodeposition can be improved in many ways by using a substantially continuous flow, for example laminar or turbulent, of electrodeposition solution between a substrate and a counter electrode, where the substrate and the counter electrode are positioned in close proximity, for example on the order of millimeters or less, to each other while the plating current is applied. Apparatus for carrying out methods of the invention are highlighted particularly by novel flow manifolds that allow electrodeposition in the manner described.

One embodiment is an electrodeposition apparatus for fabricating a photovoltaic cell, including: (i) a movement assembly for positioning a substrate in close proximity, for example on the order of millimeters or less, to a counter electrode during electrodeposition; and (ii) a flow manifold configured to flow an electrolyte between the substrate and a counter electrode and continuously supply electrolyte between the plating surface of the substrate and the counter electrode; where the counter electrode is positioned on, or an integral component of, the flow manifold. Apparatus described herein find particular use when employing a substrate that is a continuous sheet type substrate so that improved mass production of thin films is realized. Several flow manifold embodiments are described in more detail below.

Another embodiment is an electrodeposition method including: (i) flowing an electrolyte between a substrate and a counter electrode using a flow manifold that supplies a substantially continuous supply of electrolyte to the substrate while the plating surface of said substrate is in close proximity, for example on the order of millimeters or less, to the counter electrode; and (ii) applying a plating potential between the substrate and the counter electrode; where the counter electrode is configured to substantially span at least one dimension of the substrate and is positioned on, or an integral component of, the flow manifold. Particular aspects of methods of the invention are described below.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 depicts a cross-sectional view of a solar cell photovoltaic stack structure.

FIG. 2 depicts a conventional photovoltaic stack formation scenario.

FIG. 3 depicts a conventional electrodeposition apparatus for solar cell fabrication.

FIG. 4 depicts a perspective view of a flow manifold in accord with embodiments of the invention.

FIGS. 5A and 5B depict a cross-sectional side and front view, respectively, of an electrodeposition apparatus in accord with embodiments of the invention.

FIG. 6 depicts a perspective view of another flow manifold in accord with embodiments of the invention.

FIG. 7 depicts a perspective view of another flow manifold in accord with embodiments of the invention.

FIG. 8A depicts an exploded view of an electrodeposition apparatus in accord with embodiments of the invention.

FIG. 8B depicts a side cross-section view of the electrodeposition apparatus in FIG. 8A.

FIG. 9 depicts a side cross-section view of another electrodeposition apparatus in accord with embodiments of the invention.

FIG. 10 depicts a perspective view of another flow manifold in accord with embodiments of the invention.

FIG. 11 depicts a cross sectional view of an electrodeposition system which includes more than one electrodeposition apparatus in accord with embodiments of the invention.

FIG. 12 depicts a process flow for an electrodeposition method in accord with embodiments of the invention.
A. Making a Solar Cell

[0022] FIG. 1 depicts a simplified diagrammatic cross-sectional view of a typical thin film solar cell, 100. As illustrated, thin film solar cells typically include the following components: back encapsulation, 105, substrate, 110, a back contact layer, 115, an absorber layer, 120, a window layer, 125, a top contact layer, 130, and top encapsulation layer, 135.

[0023] Back encapsulation can generally serve to provide encapsulation for the cell and provide mechanical support. Back encapsulation can be made of many different materials that provide sufficient sealing, moisture protection, adequate mechanical support, ease of fabrication, handling and the like. In many thin film solar cell implementations, back encapsulation is formed from glass although other suitable materials may be used.

[0024] A substrate layer can also be used to provide mechanical support for the fabrication of the solar cell. The substrate can also provide electrical connectivity. In many thin film solar cells, the substrate and back encapsulation are the same. Glass plate is commonly used in such instances. Where electrical connectivity is also desired, glass coated with a transparent conductive coating can be used.

[0025] A back contact layer can be formed from a thin film of material that provides one of the contacts to the solar cell. Typically, the material for the back contact layer is chosen such that the contact resistance for the electrons/holes flowing from/to the absorber layer is minimized. This result can be achieved by fabricating an ohmic or a tunneling back contact layer. This back contact layer can be formed from many different materials depending on the type of thin film solar cell. For example, in copper indium gallium diselenide (CIGS) solar cells, this layer can be molybdenum. In cadmium telluride (CdTe) thin film solar cells, this back contact layer can be made, for example, of nickel or copper. These materials are merely illustrative examples. That is, the material composition of the back contact layer is dependent on the type of absorber material used in the cell. The thickness of a back contact layer film is typically in the range of a few microns.

[0026] The absorber layer is a thin film material that generally absorbs the incident photons (indicated in FIG. 1 by the squiggly arrow lines) and converts them to electrons. This absorber material is typically semiconducting and can be a p-type or an n-type semiconductor. An absorber layer can be formed from, for example, CIGS, CdTe or amorphous silicon. The thickness of the absorber layer depends on the semiconducting material, and is typically of the order of microns, varying from a few microns to tens of microns.

[0027] A window layer is also typically a thin film of semiconducting material that creates a p-n junction with the absorber layers and, in addition, allows the maximum number of photons in the energy regime of interest to pass through to the absorber layer. The window layer can be an n or p-type semiconductor, depending on the material used for the absorber layer. For example, the window layer can be formed from a cadmium sulphide (CdS) n-type semiconductor for CdTe and CIGS thin film solar cells. The thickness of this layer is of the order of microns.

[0028] A top contact is typically a thin film of material that provides one of the contacts to the solar cell. The top contact is made of a material that is transparent to the photons in the energy regime of interest for the solar cell. This top contact layer is typically a transparent conducting oxide (TCO). For CdTe, CIGS, and amorphous silicon thin film solar cells, the top contact can be formed from, for example, indium tin oxide (ITO) or doped zinc oxide (ZnO). The top contact layer thickness can be of the order of tens of microns.

[0029] A top encapsulation layer can be used to provide environmental protection and mechanical support to the cell. The top encapsulation is formed from a material that is highly transparent in the photon energy regime of interest. This top encapsulation layer can be formed from, for example, glass.

[0030] Thin film solar cells are typically connected in series, in parallel, or both, depending on the needs of the end user, to fabricate a solar module or panel. The solar cells are connected to achieve the desired voltage and current characteristics for the panel. The number of cells connected together to fabricate the panel depends on the open circuit voltage, short circuit current of the cells, and on the desired voltage and current output of the panel. The interconnect scheme can be implemented, for example, by laser scribing for isolation and/or interconnection during the process of the cell fabrication. Once these panels are made, additional components such as bi-pass diodes, rectifiers, connectors, cables, support structures etc. are attached to the panels to install them in the field to generate electricity. Installations can be, for example, in households, large commercial building installations, large utility scale solar electricity generation farms and in space, for example, to power satellites and space craft.

[0031] As mentioned above, electrodeposition is an attractive methodology for depositing various layers of thin film solar cells. Processes have been developed for the deposition of the back contact, absorber, window and top contact layers using electrodeposition.

[0032] Solar cell photovoltaic stacks are conventionally constructed in an order starting from, for example, a top encapsulation layer, a top contact layer, a window layer, an absorber layer, a back contact layer and so on, that is, in an order opposite of the description of the layers with reference to FIG. 1.

[0033] FIG. 2 shows a diagrammatic illustration of conventional photovoltaic stack formation. For illustration purposes, FIG. 2 is described in terms of CdTe-based solar cells. The process starts with the top encapsulation layer, and the cell stack is built by subsequent depositions of top contact layer, window layer, absorber layer, etc. The order of fabrication is indicated by the heavy arrow in FIG. 2. Other layers may be formed in addition to the described layers and formation of some of the described layers is optional, depending on the desired cell stack structure.

[0034] Referring again to FIG. 2, the TCO-coated glass (for example, the top encapsulation layer 205 and top contact layer 210) can be initially cleaned, dried, cut to size, and edge sealed. Float glass with transparent conductive oxide coatings, for example indium tin oxide, fluorinated tin oxide and doped zinc oxide, are commercially available from a variety of vendors, for example, glasses sold under the trademark TEC Glass™ by Pilkington of Toledo, Ohio, and SUNGATE™ 300 and SUNGATE™ 500 by PPG Industries of Pittsburgh, Pa. TEC Glass™ is a glass coated with a fluorinated tin oxide conductive layer. A wide variety of solvents, for example deionized water, alcohols, detergents and the like, can be used for cleaning the glass. As well there are many commercially available industrial-scale glass washing apparatus appropriate for cleaning large substrates, for example,
Lisect™ (a trade name for a glass washing apparatus and process available from (LISEC Maschinenbau Gmbh of Seitenstetten, Austria).

Once the ITO coated glass is cleaned, a CdS layer, 215, may then be deposited, for example, by using an aqueous solution of, for example, a cadmium salt and elemental sulfur composition. The solution does not have to be aqueous. That is, other solvents, such as dimethylsulfoxide (DMSO), can be used. This deposition can be done using electrodeposition. For electrodeposition, the ITO coated glass can form one of the electrodes. The other electrode can be, for example, made of graphite, and the electrolyte can be, for example, a DMSO solution of a cadmium salt and elemental sulfur. Potential is applied between the electrodes so that CdS is deposited from the solution onto the ITO coated glass substrate. Another method of depositing the CdS layer is chemical deposition, for example via wet chemistry or dry application such as CVD. The CdS deposited is an n-type semiconductor and its thickness is typically between 500 Å and 1 μm. Subsequent to the deposition, the layer can then be annealed, for example under an inert atmosphere such as argon, to achieve film densification and grain growth to improve the electrical and mechanical properties of the CdS film.

A cadmium telluride layer, 220, can then be electrochemically deposited on the CdS/TCO/Glass stack (now a substrate for electrodeposition), for example, from an acidic or basic medium containing a cadmium salt and tellurium oxide. In this process, the CdS/TCO/Glass substrate forms one of the electrodes and platinum or other materials can be used as the other electrode. The electrolyte can contain an acidic or basic medium, in solvents such as water, DMSO or other solvents, with a cadmium salt and tellurium oxide, for example. Films of thickness ranging from 1 to 10 μm are typically deposited. Cadmium telluride films may then be annealed at approximately 500°C in an air or oxygen or CdCl₂ environment so as to improve the electrical properties of the film and also to convert the CdTe film to a p-type semiconductor. It is believed that these methods optimize grain size and thus improve the electrical properties of the films.

After this CdTe deposition and annealing, a laser scribing process is typically performed to remove CdS and CdTe from specific regions (not shown). In this scribing operation, the solar panel is utilized such that CdTe and CdTe are ablated from specific regions of the solar panel. However, the conductive oxide (e.g., Al doped ZnO or ITO) is not removed by the laser scribe.

A back contact layer, 225, can then be deposited on the CdTe layer, using for example sputtering or electrodeposition. For example, copper, nickel and/or other metals, alloys and composites can be used for the back contact layer. This back contact fabrication step can be followed by an anneal, for example, at temperatures of between about 150°C and about 200°C, to form an ohmic contact. The back contact layer can cover the CdTe layer and also fill the vias (not shown) created in the CdTe/CdS layer by the laser scribing process.

After back contact layer deposition and annealing, laser scribing can typically be used to remove back contact layer material from specific areas, but the CdTe layer is not etched away in this process. This removal step can complete the process for isolation and interconnecting the solar cells in series in the solar panel/module.

After the deposition of the back contact layer, an encapsulation layer, 230, can be applied, for example, using ethylvinyl acetate (EVA). Encapsulation protects the photovoltaic stack. Glass, 235, can be added for further structural support (and protection) of the stack.

The above described fabrication process represents a brief outline and many variants of this process can be employed for the fabrication of CdTe thin film solar cells. For other types of thin film solar cells, different chemicals, etc. can be employed. In this description, example process steps have been described for illustrative purposes. Other steps would typically include additional details of the laser scribing and ablation steps employed for the fabrication of the interconnect schemes and cell isolations, multiple clean and drying steps between the different layer depositions and the like. Values for the layer thicknesses, anneal temperatures, chemical composition etc. described are merely illustrative. These values can vary across a wide range as processes are optimized for many different output variables.

FIG. 3 is a simplified cross-sectional illustration of a conventional electrodeposition apparatus, 300, that employs a continuous substrate. So as not to complicate the description, other components of the equipment, such as the electronics for control systems, for applying potentials to the electrodes, chemical handling system for the electrolyte etc., are not shown, but would typically be included in the system. The dimensions of the different components of the system can vary across a large range depending on the application for which the equipment is designed. FIG. 3 is a schematic of equipment that is used in conventional electrodeposition of various layers for solar cell fabrication on a continuous substrate. As shown, apparatus 300 includes a large tub, 305, which holds the electrolating solution, 310, and through which a continuous substrate, 315, is passed. Deposition on the substrate is achieved by application of an electric potential between the substrate, for example a metal foil, and a counter electrode, 320. A large tub typically contains the electrolating solution, counter electrode 320, and a mechanism, for example rollers, 325, for moving the substrate through the electrolating zone etc. The moving foil is the substrate on which deposition takes place. This foil also forms one of the electrodes of the electrolating system. The foil electrode can be made of a wide variety of materials, but generally will be electrically conductive, chemically compatible with the electrolytic solution. For example, the foil or substrate can be made of aluminum, nickel, steel and the like.

The counter electrode is the second electrode in the system and is typically immersed in the electrolating solution. This counter electrode can be made of a large variety of materials. Typically, the counter electrode is electrically conductive and chemically compatible with the electrolating solution. For example, the counter electrode may be formed from materials, such as platinum and/or graphite.

Conventional electrodeposition apparatus that employ a continuous substrate will typically include a mechanism for moving the substrate through the active electrolating zone. This movement mechanism may be in the form of rollers, 325. These rollers are used to move the substrate through the system and the electrolating and over the counter electrode to enable electrolating deposition. Substrate 315 is curled (or bent) as it passes over each roller, in this example the foil substrate is bent four times as it passes into and out of the electrolating bath and on to further processing steps. If any of these rollers are immersed in the electrolate or are in contact
with it, care is typically taken to ensure that the roller material of construction is chemically compatible with the electroplating solution.

[0045] The composition of the electrolyte depends on the material to be deposited. Examples of electroplating solutions that might be used for fabricating different layers of the CdTe solar cell are described above in relation to FIGS. 1 and 2.

[0046] Conventional apparatus, such as that described in relation to FIG. 3, can suffer from some significant drawbacks. One drawback is maintenance, for example, conventional electrodeposition equipment requires immersion of moving parts of the equipment in the electroplating solution. Electroplating solutions can have harsh, caustic chemicals, which cause degradation of these parts and create maintenance challenges. These immersed parts also have to be fabricated using materials that are compatible with these harsh chemicals, which can raise the cost of the equipment significantly.

[0047] Another drawback of conventional electrodeposition apparatus is related to chemical consumption. In a typical implementation of electrodeposition equipment the chemical consumption can be very high. First, the chemical is held in a large bath, and it is challenging to replenish the chemical in-situ to maintain the chemical concentrations of the depositing species. Second, chemical deposition in this configuration can also occur on the wall of the tub and on the immersed parts of the equipment. This non-specific or extraneous deposition increases the chemical consumption and also increases the cost and complexity of maintenance. Third, in conventional bath-type systems it is difficult to prevent deposition on both sides of the continuous substrate, which is undesirable in many applications and uses excess electrolyte solutions. Finally, use of large quantities of potentially toxic chemicals can also present an increased safety hazard and increase the cost of running the equipment to appropriately mitigate this risk.

[0048] Another drawback of conventional electrodeposition apparatus is related to deposition uniformity. Achieving deposition uniformity in this configuration poses significant challenges, for example, achieving a substantially parallel plate configuration is difficult in conventional apparatus. This can create edge effects and lead to non-uniform deposition. It is also difficult to maintain uniform substrate and solution temperature, and uniform substrate potential, further negatively impacting the deposition uniformity. It is also challenging to provide uniform solution agitation, while maintaining a flat substrate, since the foil is flexible.

[0049] Yet another drawback of conventional electrodeposition apparatus is related to modularity and interchangeability. In the conventional implementation of the equipment, it is challenging to use the same equipment for different processes. To be able to use the equipment for different processes, the materials compatibility of the immersed parts to the different chemicals has to be evaluated for each application. Different processes have different deposition rates and layer thickness requirements, which require flexibility in the variables used to achieve these outcomes, for example, the length of the electrodes and/or the rate at which the substrate is moving.

[0050] With conventional apparatus, it is not readily feasible to change the rate of the motion if the process consists of multiple depositions. In conventional implementations, it is challenging to change the length of the electrode since that would require changing the size of the bath etc. or significantly underutilizing the bath and the chemical by designing the bath for the longest deposition in the process flow. Also, by requiring that the substrate be directed into, and out of, a bath via a system of rollers, the substrate and its newly deposited film are subjected to bending over at least two rollers, four rollers in the example depicted in FIG. 3. If multiple layers were deposited using one or more conventional electrodeposition baths and a continuous substrate, the photovoltaic stack formed on the substrate is subjected to multiple bends over many rollers which can negatively affect the ultimate performance of the stack.

B. Apparatus and Methods

[0051] For illustration purposes only, electrodeposition is sometimes described herein as being used in the fabrication of CdTe-based solar cells although electrodeposition can be used to fabricate any number of other types of solar cells or other types of thin films products and/or devices. That is, the invention is not limited to this exemplary electrodeposition chemistry.

[0052] The inventors have found that many of the drawbacks of conventional electrodeposition apparatus, for example as described in relation to FIG. 3, can be overcome using methods and apparatus in accord with embodiments of the invention. More specifically, and in very general terms, instead of immersing the substrate in a volume of electrolyte, a flow of electrolyte is applied to a surface of the substrate. The inventors have found that novel flow manifolds in conjunction with appropriate substrate handling and electrodeposition components, such as potential source controllers and the like, appropriately configured, allow the substrate and counter electrode to be brought in close proximity to one another during plating, which provide advantages, for example, using less electrolyte, obviating the need to bend and direct the substrate into an electrolyte bath, establishing substantially parallel plate conditions for highly uniform deposition, and obviating the need for moving parts exposed to the bath. Further advantages are described below.

[0053] Various implementations of embodiments of the invention are described in more detail below. These implementations are meant to be illustrative, non-limiting examples. One of ordinary skill in the art would appreciate other variants of the following examples by reading the description herein. Various exemplary electrodeposition apparatus and methods in accord with embodiments of the invention will first be described and potential benefits of these implementations will be described thereafter.

[0054] One embodiment is an electrodeposition apparatus for fabricating a photovoltaic cell, including: (i) a movement assembly for positioning a substrate in close proximity to a counter electrode during electrodeposition; and (ii) a flow manifold configured to flow an electrolyte between the substrate and a counter electrode and continuously supply electrolyte between the plating surface of the substrate and the counter electrode; where the counter electrode is positioned on, or an integral component of, the flow manifold. In one embodiment, the movement assembly includes a drive component configured to move the substrate past the flow manifold and counter electrode during electrodeposition without substantially bending the substrate. In one embodiment, the substrate includes a continuous sheet that includes at least one of an electrically conductive material and a material having an electrically conductive coating. Conductive materials...
include, for example, aluminum, stainless steel, titanium and graphite foil. A material having an electrically conductive coating would be, for example, a glass, plastic, polymer or other substrate coated with a conductive coating, for example, a conductive oxide such as a transparent conductive oxide, for example, fluorinated tin oxide, indium tin oxide and the like.

[0055] FIG. 4 depicts a perspective of a flow manifold, 400, which is a component of an electrodeposition apparatus in accordance with one implementation of the present invention. The manifold 400 has a body, 405, and in this example, a counter electrode, 410, that is substantially planar with a top surface that is substantially even with the top surface of the manifold body 405. This is only one implementation of a flow manifold in accord with embodiments of the invention, that is, the counter electrode can be positioned on the manifold body or in this case, integral to or recessed in a surface of the flow manifold body. Referring again to FIG. 4, flow manifold 400 has an electrolyte inlet (or injection port), 415, and a used electrolyte outlet, 420. Although depicted as rectangular in shape, inlet and outlet electrolyte ports are not limited to any particular geometry. As well, there may be, for example, a series of inlets and outlets that serve the same purpose as a single inlet and/or outlet. During electrodeposition, a substrate, in this example a continuous sheet substrate 425, and counter electrode 410 are brought within close proximity (as indicated by the heavy double-headed vertical arrow) of each other. In one embodiment, the counter electrode and the substrate plating surface are substantially parallel planar. In one embodiment, the counter electrode and the substrate are between about 1 mm and about 25 mm apart during electrodeposition, in another embodiment between about 2 mm and about 10 mm apart during electrodeposition, in yet another embodiment between about 2 mm and about 5 mm apart during electrodeposition. In another embodiment the counter electrode and the substrate are between about 1 mm and about 5 mm apart during electrodeposition, in another embodiment between about 1 mm and about 3 mm apart, in yet another embodiment between about 1 mm and about 2 mm apart. In yet another embodiment, the counter electrode and the substrate are between about 0.5 mm and about 2 mm apart.

[0056] Although certain embodiments are described as having a substantially parallel planar orientation between substrate and counter electrode, the two electrodes can be non-parallel, before and/or during plating. Analogous to, for example, the semiconductor arts, controlling the orientation of a plating substrate with respect to the surface of an electrolyte during entry into an electrolyte and/or during an electroplating process can be beneficial. For example, bubbles can be entrapped on the plating underside of a plating substrate upon immersion into the electrolyte. Bubbles sticking to the surface of a substrate during plating can produce voids in the deposited film. Bubbles can be so entrapped specifically when the substrate is immersed in a horizontal orientation (that is, parallel to a plane defined by the surface of the electrolyte) along a vertical immersion trajectory. If the substrate surface is introduced into the electrolyte on a trajectory normal to the surface of the electrolyte, i.e. the substrate is angled before entry into the electrolyte, then entrainment of bubbles can be avoided or at least minimized. Thus in one embodiment, apparatus allow for angled immersion into a continuous flow of electrolyte from the manifold. In other embodiments, the substrate's orientation can be adjusted actively during immersion or during electrodeposition. Active angle adjustment refers to changing the angle of the substrate relative to a theoretical plane of the flowing electrolyte across the surface of the flow manifold at any time during positioning or electrodeposition. This provides flexibility in various electrodeposition scenarios. In a typical, but non-limiting, example, however, laminar electrolyte flow (as described in more detail below) is employed which aids in removing any bubbles that could cause film defects.

[0057] Referring again to FIG. 4, substrate 425 and counter electrode 410 are brought into close proximity of each other, and an electrolyte flow is established between them. The direction of the flow in this example is indicated by the dotted arrows, first emanating from inlet 415, and then exiting into outlet 420. In this example, a continuous flow can be produced (via appropriate reservoirs and pumps not depicted) that flows into the void between the substrate and the counter electrode, between the substrate and the counter electrode, and drains via outlet 420. In one example, the flow pattern is substantially laminar. The dotted arrow above substrate 425 indicates the direction of movement of the substrate relative to the flow manifold 400. In one embodiment, the continuous sheet substrate is moved continuously during electrodeposition, in another embodiment the substrate is periodically repositioned in order to electrodeposit on an area of the substrate that has no film yet deposited. In other embodiments the electrolyte flow is turbulent.

[0058] In certain embodiments, the substrate continuously moves relative to the counter electrode of the flow manifold. In a specific implementation, the length of the manifold, "L," as depicted in FIG. 4, will depend on the speed at which the substrate is moving, deposition rate of the electrodeposition process, and the thickness of the material to be deposited. The length of the electrode can be given by the formula:

$$L = \frac{R \times S \times T}{R}$$

where L = length of the electrode, T = thickness of the film to be coated, R = rate of deposition and S = speed of the substrate motion. If, for example, the thickness of the layer to be deposited is 1 μm, the substrate is moving at a speed of 1 foot/minute and the deposition rate of the layer is 1 μm/minute, then the length of the electrode would be: L = (1 μm x 1 foot/minute)/(1 μm/minute) = 1 foot. In one embodiment, the counter electrode substantially spans the width of the substrate as the substrate passes by the counter electrode during electrodeposition. FIG. 4 depicts the counter electrode width as "W." A single counter electrode need not be used, but rather two or more appropriately spaced and/or patterned counter electrodes can work as well, and are included as an alternative embodiment wherever "a counter electrode" is described herein.

[0059] FIGS. 5A and 5B show side and front cross sections, respectively, of an electrodeposition system, 500, for electroplating on a continuous substrate in accordance with a specific implementation of the present invention.

[0060] Referring to FIG. 5A, apparatus 500 has a flow manifold which includes a body, 505, which has an electrolyte inlet, 515, and outlet, 520. The flow of electrolyte (540 as indicated in FIG. 5A) during electrodeposition is indicated by the dashed arrow going from 515 to 520. A substrate, 525, for example a foil, is moved by a roller, 530, which can also provide temperature control and hold the substrate flat, for example, via an applied vacuum to the backside of substrate 525. Roller 530’s movement is indicated by curved dashed arrows on roller 530, where substrate 525 is delivered to roller 530 from a roll of substrate or the like. Roller 530 can also
protect the backside of substrate 525 such that electrodeposited material is applied only to one side of the substrate. A roller for moving the substrate is typical, but not necessary. In one embodiment, the roller is replaced, for example, by a skid structure that also may apply potential, provide temperature control and hold the substrate flat as described in relation to the roller. In the skid embodiment, the substrate is pulled through or between the skid and the counter electrode. In a typical process, a potential is applied between substrate 525 and a counter electrode, 510. In this example, counter electrode 510 is recessed into manifold body 505 such that the top surface of the counter electrode is flush with the top surface of the manifold body. The substrate moves over the manifold that is used to inject electroplating solution from one end and evacuate such solution out the other end of such manifold. The potential difference between the substrate and second electrode cause a material, 535, from the electrolytic solution to deposit on the surface of substrate 525 opposite that touching roller 530 as substrate 525 moves past, and in close proximity to, the counter electrode. In one embodiment, the substrate moves continuously, in another embodiment, the substrate is moved periodically to electrodeposited while the substrate is not moving. FIGS. 5A and 5B show one possible implementation of this equipment. Although one possible implementation is shown, other implementations are also possible. For example, the equipment could be inverted so that the manifold is above the moving substrate, or the components could be vertically oriented or at some angle to take advantage of gravity, for example, to drive and/or guide electrolyte flow and/or to take into account other fabrication advantages.

[0061] One or more potential sources apply a potential difference between the substrate (for example, via the movement mechanism) and the electrode so that material from the electrolytic solution is deposited on the one surface of the substrate. The one or more potential sources can take any suitable form such as a direct current source, for example, an adjustable or fixed current source. In this embodiment, the substrate continuously moves adjacent to the electrode so that a material from the solution is deposited in a thin film across the entire first surface of the substrate.

[0062] Manifold body 505 can be constructed from many different materials such as polytetrafluoroethylene (PTFE, also known as Teflon which is registered trademark of E.I duPont de Nemours and Company, of Wilmington, Del.), fluorinated ethylene propylene (FEP), ethylene tetrafluoroethylene (ETFE), ethylene chlorotrifluoroethylene (ECTFE), perfluoropolyethylene fluoride (PVDF), tetrafluoroethylene hexafluoropropylene vinylidene fluoride (THV), polyetheretherketone (PEEK™ is a registered trademark of Victrex of Lancashire, UK), polyetherimide (PEI) and the like. Preferably, these materials are chemically resistant, easy to machine, and electrically insulating. Fluoropolymers are generally well suited for these criteria. Counter electrode 510 can be made from many different materials. The different electrode materials that can be used for fabrication of the different layers of the CdTe solar cell, for example, are described above.

[0063] Although some embodiments describe the relationship between the counter electrode and the substrate where the counter electrode substantially spans the width of the substrate, any suitable dimensions for the counter electrode can be used. In one embodiment, the dimensions are selected so that the counter electrode is wider than the substrate being coated so that a parallel plate configuration can be maintained and the edge electrical field effects can be minimized. FIG. 5A illustrates a counter electrode wider than the substrate passing over it.

[0064] The manifold may optionally include capabilities for pre-cleaning of the substrate and rinsing and drying. For example, a nitrogen, argon and/or air curtain and/or knife can be added at one end of the manifold. In one implementation, the gas or gases would be plumbed into the manifold and blown onto the substrate to dry it. Similarly for pre-cleaning and rinsing, de-ionized water or other solvent can be sprayed onto the substrate through the manifold. Any one of, and combinations of, pre-cleaning, rinsing, and drying can be done before the substrate enters the electrodeposition zone and after it exits the electrodeposition zone.

[0065] Although a roller provides a movement mechanism for moving the substrate/foil, in one implementation of the present invention, other movement mechanisms may also be utilized. Additionally, but not necessarily, a heater can be attached to the movement mechanism for heating the substrate. Also, vacuum or suction can be provided to the roller to hold the substrate flat onto the roller. Some other holding mechanism can also be employed to hold the substrate on the movement mechanism. The roller can also be used for applying potential to the substrate. In one embodiment, this potential could be ground with respect to the counter electrode.

[0066] An electrolytic solution can have different compositions, which depends on the process requirements for the layer being deposited. Examples of electrolytic solutions that can be employed for depositing different layers for the CdTe solar cell are discussed above.

[0067] The foil or substrate can take the form of a continuous substrate on which the deposition is to be performed and can also act as one of the electrodes of the system. Different types of foils or substrates can be used. Examples of the different types of electrodes and the requirements for the foils are discussed above. The substrate may also take the form of a glass sheet coated with a TCO (which serves as the electrode). In one embodiment, the substrate is such a glass sheet. In the other embodiment, the glass sheet is continuous.

[0068] Referring to FIG. 5B, the solution is contained between the substrate and counter electrode 510. Around the perimeter of the gap between the two electrodes fluid surface tension can be employed to constrain the solution, that is, a swell of electrolyte is of sufficient flow, and the electrodes are close enough together, that fluid surface tension is employed for containing the solution and no additional sealing is required. Additionally, overflow channels, 545, can be constructed to contain any electrolyte that leaks out (overflow channels are not depicted in FIG. 5A, but one embodiment includes an overflow channel that encompasses at least a portion of, optionally all of, the perimeter of the flow manifold).

[0069] It is important that the electrolytic solution properly wet the two electrodes. One way to achieve this consistently is to apply the electrolytic solution under sufficient pressure. If the surface tension is not adequate to contain the solution at a desired injection pressure, seals can be also employed. Thus, one embodiment is the apparatus as described above further including one or more seals, the seals configured to channel the flow of electrolyte in order to maximize contact with the substrate and minimize the amount of electrolyte needed to produce the continuous supply of electrolyle con-
tacting the substrate during electrodeposition. For example, one or more seals may be employed to contain the electrolytic solution in the electroplating zone, and different mechanisms can be employed for such containment. Sufficient sealing can be achieved, for example, by using dams, for example made from the materials described in relation to manifold 510 or those described below in relation to sealing elements, around one or more sides of the counter electrode, on or in close proximity to the manifold body, to aid in fluid containment. In some embodiments, one or more seals are attached or in close proximity to at least one of the flow manifold and the counter electrode. In another embodiment, the one or more seals are part of a unitary manifold body.

[0070] Many different materials could be employed for this containment purpose. In one embodiment, the one or more seals include at least one of PTFE, silicone, butylrubber, and fluoroelastomers such as Viton and Kalrez (Viton and Kalrez are registered trademarks of DuPont Performance Elastomers, of Wilmington, Del.).

[0071] “Seals” for the purposes of certain embodiments need not come in contact with the substrate. That is, since the counter electrode and the substrate are in close proximity to one another, and electrolyte flow and surface tension can be used to compensate for electrolyte loss around the perimeter of the space between the electrodes, “seals” can be used to aid in containment, while not necessarily completely containing the electrolyte between the electrodes. Thus, seals can be non-contact and contact-type seals, that is, where the substrate does not touch the seal or the substrate does touch the seal. In one embodiment, non-contact seals are dams, where the substrate comes in close proximity, for example, on the order of a few millimeters, to a millimeter or less than a millimeter, to the seals but does not touch them. This close proximity need not entail actual overlap of the surfaces of the seal and the substrate, that is, the edges of each of the seal and the substrate might simply be brought in close proximity in order to minimize electrolyte loss between them. Also, in the figures seals are depicted as having a rectangular (or square) cross section. In other embodiments, invention may not be limited in this way. In one embodiment, the seals have minimal surface area at the portion of the seal that either contacts or comes in close proximity to the substrate, for example, a “tear drop,” triangular, fin or blade cross section. When the substrate comes in contact with the substrate, the material can be chosen not only to protect the substrate from damage, but also the electroplated material. Certain embodiments include one or more contact and/or non-contact seals as described in more detail below.

[0072] FIG. 6 depicts a flow manifold, 600, which has a body, 605, a counter electrode, 610, electrolyte inlet and outlets, 615 and 620, respectively, and seals 630 on either side of the counter electrode in accordance with one embodiment of the present invention. The substrate, 625, moves in the direction indicated by the dashed arrow during electrodeposition. Although not shown to scale in FIG. 6, typically the substrate will span seals 630. If seals 630 are contact seals, then the substrate would touch the seals; if non-contact seals, then the substrate would come very close, as described above, but not touch the seals. In the event there is overlap of the substrate with the seals, and therefore electrodeposition is blocked, this portion of the substrate can be trimmed off at a later stage. As this figure is not drawn to scale, one of ordinary skill in the art would appreciate that the electrodes can be very close to one another and thus seals 630 could be quite thin, for example, on the order of less than a millimeter, about a millimeter to a few millimeters thick (in the dimension between the electrodes).

[0073] Another embodiment is an apparatus as described above where the one or more seals are configured to form a flow barrier on each of the sides of the substrate parallel to direction of electrolyte flow, and a partial flow barrier on the downstream end of the flow manifold. FIG. 7 depicts a flow manifold, 700, which has a body, 705, a counter electrode, 710, an electrolyte inlet, 715, and a seal, 720, that in this example, spans three sides of the perimeter of the counter electrode. The substrate, not depicted, moves in the direction indicated by the dashed arrows during electrodeposition, that is, parallel to the counter electrode and in a direction from the inlet end of the manifold to the opposite end of the manifold. In this example the substrate will span the length and width (or close to the width in the case of edge-type non-contact sealing) of seal 720. Seal 720, whether contact-type or not, aids in containment of the electrolyte in the volume between the electrodes and within the three sides of seal 720. Seal 720 can be part of the unitary body of the manifold, or attached thereto. In this example, apertures 725 in seal 720 serves as electrolyte outlets. In one implementation, manifold 700, is part of an electrodeposition apparatus where manifold 700 is oriented vertically (or at some angle greater than zero), that is, where the electrolyte inlet is at the top and apertures 725 are at the bottom of the manifold so that gravity can be employed to aid in electrolyte containment (keeping the electrolyte from flowing toward the inlet) and flow (gravity pulling electrolyte down) between the electrodes. In this configuration, electrolyte would flow in a substantially laminar fashion between the electrodes as described above. Another embodiment is the apparatus as described in relation to FIG. 7, further including an upstream seal that forms a flow barrier on the upstream end of the flow manifold, where the electrolyte inlet is located downstream of the upstream seal.

[0074] As mentioned above, in some embodiments, there are one or more sealing members that aid in containing the electrolyte sufficiently to maintain the desired flow characteristics during electrodeposition. In some embodiments this arrangement includes sealing, via contact and/or non-contact seals, a perimeter around the counter electrode. Thus, one embodiment is an electrodeposition apparatus as described above, where one or more seals are configured to form a chamber (volume) between the substrate and the flow manifold, when the flow manifold and the substrate are engaged with, or in close proximity to, the one or more seals. In one embodiment, the electrolyte inlet and an electrolyte outlet, are each contained within the chamber during electrodeposition. In one embodiment, the perimeter is established via a single seal, where the single is a contact and/or a non-contact type seal. That is, the single seal can have portions that contact the substrate and portions that do not, depending on the flow and other requirements of the system. The single seal can be, for example, rectangular, oval, round, or any suitable shape. The single seal can be attached to at least one of the flow manifold and the counter electrode or not attached to either. In one embodiment, the single seal is configured to be periodically removed between plating operations to aid in keeping the chamber clean between electrodepositions. The seal is either cleaned for further use or replaced with a fresh seal. In one embodiment the single seal is rectangular, for example as depicted in FIG. 8A.
FIG. 8A depicts an exploded view of an exemplary electrodeposition assembly, 800, of the invention. The heavy double headed arrows indicate that the individual components of the assembly are engaged as indicated during electrodeposition. For simplicity, components such as controllers, voltage lines, fluid flow lines, pumps, reservoirs, etc. are not depicted. Assembly 800 includes a flow manifold, 805, which has an electrolyte inlet and outlet as well as a counter electrode as described above in relation to other embodiments. The dashed arrows indicate the intended flow pattern of electrolyte from the inlet, across the counter electrode and draining via the outlet. Assembly 800 also includes a rectangular seal, 810, a continuous substrate, 815, and a roller, 820. Dashed arrows also indicate intended movement patterns for the substrate and the roller which engages and moves the substrate. These components can function as described above in relation to other embodiments, but particulars of this embodiment are described in more detail below.

FIG. 8B depicts assembly 800 where the components depicted in FIG. 8A are engaged. Manifold 805 has a body 801 which includes counter electrode 802 and inlet and outlets, 803 and 804, for the electrolyte to enter and exit the system during electrodeposition. Seal 810, upon engagement with substrate 815 and manifold 805, forms a volume (or chamber) that, in this example, encompasses the perimeter of the counter electrode and the electrolyte inlet and outlet ports. Thus, once engaged and electrolyte is flowing, a laminar flow of electrolyte is established between the substrate (electrode) and counter electrode. Again, as mentioned in relation to FIG. 6, the description is not to scale, for example the distance between the electrodes can be quite small and correspondingly seal 810 can be less than a millimeter to the order of several millimeters thick. Also the cross-section of the seal may be other than rectangular, for example, a blade, triangular or teardrop and the overall shape of the seal can be other than rectangular, for example, oval, diamond, or other polygon or non-regular shape, depending upon the desired flow characteristics.

Referring again to the embodiment with respect to FIGS. 8A and 8B, seal 810 can be a contact seal, a non-contact seal or a combination of the two. In one embodiment, the perimeter seal is a contact seal (sometimes referred to as a soft seal) as described above, that makes contact with the substrate around entire perimeter of the seal. In another embodiment, the perimeter seal is purely non-contact seal as described above, where no actual contact is made with the substrate, but rather comes close enough that, along with surface tension and flow rate, there is always electrolyte between the substrate and the counter electrode sufficient for uniform film deposition during electrodeposition. In yet another embodiment, seal 810 has contact and non-contact components, for example, where the substrate comes in contact with seal 810 on the sides parallel to the direction of movement of the substrate, but does not contact seal 801 at the upstream and downstream sides of seal 810. In one implementation of this embodiment, the height (or thickness in the dimension measured between the electrodes) of seal 810 is the substantially uniform, but the substrate only touches the upstream and downstream sides, for example, because of the substrate’s limited width as compared to the perimeter seal.

Although seal 810 is depicted as separate from the manifold, it can be part of the manifold, for example, formed as a feature emanating from a unitary flow manifold body and thus could be thought of as a fluid dam. The flowing electrolyte would flow over the top edge of the dam in the absence of engagement (contact or not) with the substrate. In the case of a non-contact seal, the substrate is positioned just above (or near as where the substrate and seal edges are in close proximity but with no overlap), for example as little as a few millimeters, a millimeter or even less than a millimeter away, from the top surface of the dam, so that only minimal electrolyte escapes from the “chamber” thus formed between the electrodes and (within) the dam. Configurations such as this can be desirable, for example where minimal electrolyte flows away from the substrate, particularly in the regions close to the perimeter of the plating surface where localized eddy currents can interfere with uniform plating. In the event the seals is a contact seal, for example teflon, care has to be taken that the seal does not abrasively damage the substrate. Moreover the seals, even if contact type seals, may have perforations or outlets configured to aid in electrolyte flow patterns, for example, to aid in establishing substantially laminar flow between the electrodes. In one embodiment there are apertures in the perimeter seal, for example as depicted in FIG. 7, where the apertures are located on one or more sides, for example the two sides parallel to the direction of the substrate movement, and/or the downstream end side of the seal. These apertures can be used to tailor electrolyte flow patterns to suit the needs of the user to electrodeposit a particular film in a particular way.

Although seal 810 is depicted in FIG. 8B as contacting both the substrate and the flow manifold, this is not necessarily the case. “Engagement” for the purposes of this invention includes close proximity engagement without actual contact. Like non-contact sealing as described above in relation to the relative positioning of a surface of the seal and the substrate, non-contact sealing can also exist, either alone or in combination with substrate sealing, between a surface of the seal and the manifold. In one embodiment, the seal 810 is a rigid seal, for example made of teflon, PEEK, a teflon coated metal (or other support infrastructure) member and the like, which is suspended between the substrate and the flow manifold during engagement. Since a surface of the seal is in close proximity to the manifold, and another surface (or portion, if for example the seal has an oval or circular cross section) of the seal is in close proximity to the substrate, the volume or chamber as described above is formed, even though there is some electrolyte leaking between the small gap between each of the seal and the substrate and the seal and the manifold. Such an arrangement can create a desirable flow dynamic, for example near the substrate edges as described above, but also at the edges of the counter electrode to enhance uniform plating. Such a configuration can also be beneficial to aid in preventing buildup of materials that would otherwise deposit, for example, in corners where a seal and the manifold surface meet. Also, such configurations are beneficial because a seal that does not come in physical contact with the manifold or substrate, in this example suspended between the substrate and the manifold, can be easily interchanged and cleaned periodically.
Although FIG. 8B depicts the substrate in contact with the seal at substantially the same level both at the leading edge of the seal and at the following edge where the substrate would have a deposited film (not depicted here) thereon, this arrangement of the sealing surface with respect to the substrate is not necessary. In one embodiment, the seal surface at the following edge is lower than that at the leading edge, to compensate for the thickness of the newly deposited film on the substrate that must pass over the following edge of the seal. In some embodiments this differential height is not necessary because the seal is pliable and does not damage the substrate or deposited film, for example a soft blade seal, elastomeric and/or spring actuated seal. As mentioned, one embodiment is a combination of contact and non-contact seals. In one implementation of this combination, the leading edge of the seal can be a contact seal while the following edge is a non-contact seal, where the newly deposited film does not make contact with the following edge of the seal. One of ordinary skill in the art would appreciate that many combinations are possible without escaping the scope of the invention.

FIG. 8B and FIG. 9 depict electrodeposition assemblies in a vertical orientation. Such an orientation allows gravity to aid in producing a laminar flow (downward) from the inlet side to the outlet side of the manifold. As discussed above, embodiments of the electrodeposition apparatus are not limited to any particular orientation, however.

FIG. 9 depicts a cross sectional view of another electrodeposition assembly, 900, similar to that described in reference to FIGS. 8A and 8B, but with different configuration for the electrolyte inlet and outlet. Assembly 900 includes a manifold to a body, 905, and a counter electrode, 910. Substrate 920 is driven by roller 930 past the counter electrode as described above. In this example, seal 915 has one or more apertures, 930, in its leading side, and one or more apertures, 935, in its downstream side. One or more apertures 930 serve as the electrolyte inlet, and apertures 935 serve as the electrolyte exit from the between the substrate and the counter electrode. The apertures are in fluid communication with the appropriate plumbing (not depicted). This configuration aids in producing a substantially laminar flow by orienting the inlet and outlet flows substantially parallel to the planes of the substrate and the counter electrode. With respect to the description herein that the inlet and outlet are part of the flow manifold, this is consistent because, for example, seal 915 can be of the type that is part of a unitary body of the flow manifold. In other embodiments, the combination of (or engagement with) a sealing element and a manifold body are together part of the flow manifold.

As mentioned, neither the seal component, the electrolyte inlet or outlet, nor the manifold body, of electrodeposition apparatus in accord with embodiments of the invention are limited to any particular geometry. In embodiments with a perimeter-type seal, for example, the seal can be rectangular, oval, circular, square, triangular, or an irregular shape and have a cross section that is, for example, rectangular, circular, oval, teardrop, triangular, irregular, i.e. any suitable shape. Also as mentioned, one aspect of the invention is creation of substantially laminar electrolyte flow between the substrate and counter electrode during electrodeposition. In apparatus of the invention, flow characteristics can be achieved, for example, via manipulation of the configuration of one or more of the seal, electrolyte inlet and outlet, counter electrode, etc. as well as taking advantage of surface tension, gravity, characteristics of the electrolyte, for example viscosity, velocity, temperature and pressure.

FIG. 10 depicts a perspective view of another electrodeposition assembly, 1000, of the invention, where the seal and electrolyte ports are configured to aid in formation of substantially laminar electrolyte flow between the substrate and the counter electrode. Assembly 1000 includes a manifold with a body, 1005, and a counter electrode, 1010. Substrate 1030 (shown above the manifold) is driven by roller (not depicted) past the counter electrode as described above, and substrate 1030 spans the width of seal 1025 or at least comes in close proximity (for example non-contact sealing with or without overlap of substrate and seal). In this example, seal 1025 has a hexagonal shape (and a rectangular cross section). Electrolyte inlet 1015 and electrolyte outlet 1020 are triangular as depicted, but can be rectangular, circular, oval and the like. The hexagonal shape of seal 1025 aids in producing a substantially laminar flow by directing electrolyte flow from the inlet smoothly, via the angled sides proximate the inlet, to expand and deflect toward the downstream outlet between the substrate and counter electrode. Laminar flow can also be produced in apparatus 1000, for example, by using inlets and/or outlets that flow introduce and/or exit electrolyte from the chamber, for example, as described in relation to FIG. 9, that is, parallel to the electrode surfaces so that diversion from a vertical inlet to a horizontal flow (as depicted in FIG. 10) is avoided.

Another implementation of the sealing is where the edges of the substrate, for example a foil substrate, are bent such that it contains the electrolyte, without touching the counter electrode and causing a short. In this implementation, the area of the foil that is bent would most likely have to be trimmed and discarded after the fabrication of the solar cell stack. This two examples, distinct seals and using a portion of the substrate as a vertical sealing element, are only illustrative, non-limiting examples of apparatus components and methods for containment of the electrolyte during deposition on the substrate.

Another embodiment is a flow manifold for delivering an electroplating solution to the surface of a substrate, the flow manifold including: (i) an electrolyte inlet, the electrolyte inlet upstream of; (ii) a counter electrode, the counter electrode disposed on a surface of the flow manifold; and (iii) an electrolyte outlet, the electrolyte outlet downstream of the counter electrode; where the flow manifold is configured to supply a continuous flow of the electroplating solution from the electrolyte inlet, between the counter electrode a surface of the substrate so that electroplating can occur on the surface of the substrate, and then drain via the electrolyte outlet. In one embodiment, the flow manifold is configured to supply electrolyte while engaged with a continuous sheet substrate. In another embodiment, the flow manifold further includes a controller configured to supply the continuous flow of the electroplating solution to the continuous sheet substrate while the continuous sheet substrate is moved continuously past and in close proximity to the counter electrode. In another embodiment, the flow manifold is configured to produce a substantially laminar flow or a turbulent flow of the electroplating solution between the surface of the substrate and the counter electrode. The flow manifold can also include one or more seals configured to channel the flow of electroplating solution in order to maximize contact with the surface of the substrate and minimize the amount of plating solution needed to produce the continuous flow of the electroplating solution.
contacting the substrate during electrodeposition. The flow manifold can also include one or more overflow channels for collecting used electrolyte. The one or more seals can be configured to form a flow barrier on each of the sides of the substrate parallel to the direction of electroplating solution flow, and a partial flow barrier on the downstream end of the flow manifold, and optionally include an upstream seal that forms a flow barrier on the upstream end of the flow manifold. Thus in another embodiment, the one or more seals are configured to form a chamber or volume between the surface of the substrate and the flow manifold when the flow manifold and the substrate are engaged with the one or more seals. In one embodiment, the flow manifold has a single seal. In a more specific embodiment, the seal is rectangular. Manifold embodiments can also include pumps and valves configured to recirculate the electrolyte when flowing but while electrodeposition is not taking place. That is, an embodiment where the apparatus is configured to recirculate the electrolyte through the manifold until electrodeposition commences and then the used electrolyte is no longer recirculated through the manifold, but rather diverted for other dispositions, for example, reconstitution or to a waste stream.

Another, more specific, embodiment is an electrodeposition apparatus for fabricating a photovoltaic cell on a continuous substrate, the apparatus including: (i) a movement assembly for positioning a substrate between about 2 mm and about 5 mm from a counter electrode during electrodeposition; (ii) a flow manifold configured to flow an electrolyte between the substrate and a counter electrode and continuously supply electrolyte between the plating surface of the substrate and the counter electrode; (iii) a drive component configured to move the continuous substrate past the flow manifold and the counter electrode during electrodeposition without substantially bending the substrate; and (iv) one or more seals configured to channel the flow of electrolyte in order to maximize contact between only a plating side of the continuous substrate and the counter electrode; where the counter electrode is positioned on, or an integral component of, the flow manifold and the continuous substrate comprises at least one of an electrically conductive material and a material having an electrically conductive coating.

The embodiments described above are not limited to single apparatus working on, for example, a continuous substrate. One embodiment is an electrodeposition system including at least two of the flow manifolds as described herein in series that operate on a single continuous substrate.

FIG. 11 depicts system, 1100, for electrodepositing multiple layers on a substrate. In this example, three electrodeposition apparatus, 1110, 1120 and 1130, are arranged so that when substrate, 1140, passes from one apparatus to the next, a first layer is electrodeposited on the substrate, then a second layer is deposited on the first layer, and then a third layer is deposited on the second layer. The continuous substrate can move through the apparatus non-stop or stop periodically for electrodeposition or other processing. In one embodiment, the substrate moves continuously through each of the electrodeposition stations. In the example depicted in FIG. 11, each of the first, second and third layers have different compositions and are therefore deposited using different electrodeposition chemistries. Although depicted as identical, each of the deposition apparatus, 1110, 1120 and 1130, can be of any configuration consistent with the invention as described. Electrodeposition apparatus in accord with embodiments of the invention allow for many advantages including extreme flexibility when depositing multiple layers on a single substrate, i.e., they are modular and can be interchangeable depending upon the desired outcome. For example, not only can the chemistries vary across different electrodeposition apparatus, but also the individual apparatus can be unique (or not) according to the variables described, such as sealing configuration, shape, contact-type or not, flow parameters, and the like.

Note also in FIG. 11, as indicated by the heavy arrows above and below the substrate that there can be pre- and post-processing of the substrate’s newly deposited layer in between (and after the last) deposition stations. Thus, there can be other apparatus positioned in between (or prior to the first) electrodeposition apparatus and, for example, process the substrate prior to entering the first station (for example preheating, prewetting) or process a newly added film prior to entering a subsequent station, for example, a baking step, a baking and/or anneal step, and an addition of one or more intervening layers, etc. Metrology can also be performed on the layers in between and/or after the electrodeposition stations.

Also, since the individual electrodeposition apparatus can be aligned, for example as depicted in FIG. 11, the substrate can be processed in multiple apparatus without having to be bent, which allows for greater process control and film stability and uniformity. Once the desired deposition is complete, further post-processing of the substrate, for example, substrate can then be cut to form individual solar cells which can then be tested and sorted based on their performance, followed by a bonding operation, and an encapsulation operation to form the solar panel. The solar cells can be tested for efficiency, open circuit voltage, short circuit current and the like. The solar cells can be binned according to, for example, their performance characteristics and appropriately used for fabricating the solar panels. Further details of serial type operation on a continuous substrate is described in U.S. Provisional Application Ser. No. 61/171,007, which is incorporated by reference herein for all purposes.

As one of ordinary skill in the art would appreciate, the electrodeposition apparatus in accord with embodiments of the invention may also include a controller system for managing the different components of the system. By way of examples, the controller may be configured or programmed to select the potential difference that is applied between the substrate and the electrode, control the electrolytic flow rate and fluid management, control the movement mechanism, and the like. Any suitable hardware and/or software may be utilized to implement the controller system. For example, the controller system may include one or more microcontrollers and microprocessors such as programmable devices (for example, complex programmable logic devices (CPLDs) and field programmable gate arrays (FPGAs)) and unprogrammable devices such as gate array application specific integrated circuits (ASIC’s) or general-purpose microprocessors and/or memory configured to store data, program instructions for the general-purpose processing operations and/or the inventive methods described herein.

Another embodiment is an electrodeposition method including: (i) flowing an electrolyte between a substrate and a counter electrode using a flow manifold that supplies a continuous supply of electrolyte to the substrate while the plating surface of the substrate is in close proximity to the counter electrode; and (ii) applying a plating potential between the substrate and the counter electrode; where the
counter electrode is configured to substantially span at least one dimension of the substrate and is positioned on, or an integral component of, the flow manifold.

[0094] FIG. 12 depicts a process flow, 1200, for this method embodiment. First, an electrolyte flow is established between a substrate and a counter electrode, where the substrate and counter electrode are in close proximity (as described above in relation to apparatus of the invention) using, for example, a flow manifold as described above, see 1210. Then a plating potential is between the substrate and counter electrode so that electrodeposition of a species from the electrolyte to the substrate is achieved, see 1220. Then the process flow ends. In one embodiment, the method further includes moving the substrate continuously past the counter electrode during electrodeposition, where the substrate includes a continuous sheet, the continuous sheet including at least one of an electrically conductive material and a material having an electrically conductive coating.

[0095] In another embodiment, the method further includes: (iii) electrodeposition material onto the substrate while the substrate is stationary; (iv) repositioning the substrate so that an area without electrodeposited material is positioned for electrodeposition; and (v) electrodepositing material onto the area; where the substrate is a continuous sheet including at least one of an electrically conductive material and a material having an electrically conductive coating. In one embodiment, close proximity means the counter electrode and substrate are positioned between about 2 mm and about 25 mm apart during electrodeposition, in another embodiment between about 2 mm and about 10 mm apart during electrodeposition, and in another embodiment between about 2 mm and about 5 mm apart during electrodeposition. In yet another embodiment, close proximity means the counter electrode and substrate are positioned between about 1 mm and about 2 mm apart. In another embodiment, the counter electrode and substrate are between about 0.1 mm and about 2 mm apart. In one embodiment, flowing an electrolyte between the substrate and the counter electrode includes producing a substantially laminar flow or a turbulent flow of the electrolyte between the substrate and the counter electrode. In one embodiment the flow is substantially laminar. In another embodiment, the method further includes employing one or more seals configured to channel the flow of electrolyte in order to maximize contact with the substrate and minimize the amount of electrolyte needed to produce the continuous supply of electrolyte contacting the substrate during electrodeposition.

[0096] In a more specific embodiment, the one or more seals are configured to form a chamber (or volume) between the substrate and the flow manifold when the flow manifold and the substrate are engaged with the one or more seals; the flow manifold further including an electrolyte inlet configured to supply electrolyte to the chamber and an electrolyte outlet configured to drain used electrolyte from the chamber during electrodeposition. In another embodiment, the one or more seals are configured to form a flow barrier on each of the sides of the substrate parallel to direction of electrolyte flow, and a partial flow barrier on the downstream end of the flow manifold, and optionally an upstream seal that forms a flow barrier on the upstream end of the flow manifold, where the flow manifold further includes an electrolyte inlet, the electrolyte inlet located downstream of the upstream seal. The seals can be attached to at least one of the flow manifold and the counter electrode. In the chamber or volume embodiments, the one or more seals include a single rectangular seal or a seal of a shape as described in relation to the apparatus above.

[0097] Certain embodiments of the present invention have several associated advantages. One advantage can be lower maintenance than conventional electrodeposition apparatus. For example, in embodiments employing a continuous substrate, only one surface of the substrate comes in contact with the electrolyte, and this arrangement significantly mitigates the chemical compatibility issues for the parts and also reduces the cost of the equipment significantly. Maintenance of this equipment is easy since only a relatively small number of parts of the equipment are exposed to harsh chemicals.

[0098] Another advantage can be lower chemical consumption than in conventional systems. In one implementation, the chemical consumption is reduced significantly since only a thin film of liquid is used for deposition and only one surface of the substrate, along with the counter electrode, is in contact with the electroplating solution.

[0099] Another advantage can be deposition uniformity. Since a thin film of electrolyte is constantly flowing past the electrodes, a significantly better chemical uniformity can be achieved by replenishing the chemicals depleted during the deposition process. In one implementation, a substantially parallel plate configuration can be achieved, for example by making the manifold electrode larger than the continuous substrate, for example as depicted in FIG. 5B. This is only one possible arrangement to achieve this result. Many other variations of this implementation can achieve a parallel plate configuration. In the illustrated example, the substrate temperature, potential, and flatness can be controlled very precisely since the substrate is in contact with the roller. Also, the temperature of the electrolyte can be controlled very precisely since it is a thin film of flowing electrolyte and heat loss due to dissipation at the edges represents only a very small percentage of total liquid volume.

[0100] Yet another advantage over conventional apparatus and methods can be modularity and interchangeability. Certain implementations lend themselves very well to modularity and interchangeability. The same manifold and infrastructure can be used for multiple depositions since the chemical compatibility of the parts is not an issue because only the electrodes are wetted. The manifolds in this implementation can be sized for the fastest deposition in a multiple deposition line and for longer depositions multiple manifolds can be used to achieve the targeted thickness. Other advantages with respect to modularity are described above in relation to FIG. 11.

[0101] Certain embodiments of the electrodeposition apparatus and methods described herein, for example on continuous substrates, overcome most of the challenges associated with conventional methods of electrochemical deposition, significantly reducing the cost of the equipment, reducing the chemical consumption, enhancing the maintainability, deposition uniformity, and it is modularity and interchangeability.

[0102] Although the foregoing invention has been described in some detail for purposes of clarity of understanding, it will be apparent that certain changes and modifications may be practiced within the scope of the appended claims. Therefore, the present embodiments are to be considered as illustrative and not restrictive and the invention is not to be limited to the details given herein, but may be modified within the scope and equivalents of the appended claims.
What is claimed is:
1. An electrodeposition apparatus, comprising:
   (i) a movement assembly for positioning a substrate in close proximity to a counter electrode during electrodeposition; and
   (ii) a flow manifold configured to flow an electrolyte between the substrate and a counter electrode and continuously supply electrolyte between the plating surface of the substrate and the counter electrode; wherein the counter electrode is positioned on, or an integral component of, the flow manifold.
2. The apparatus of claim 1, wherein the movement assembly is configured to move a continuous sheet type substrate, said continuous sheet type substrate comprising at least one of an electrically conductive material and a material having an electrically conductive coating.
3. The apparatus of claim 2, wherein the movement assembly comprises a drive component configured to move the continuous sheet type substrate past the flow manifold and counter electrode during electrodeposition without substantially bending the substrate.
4. The apparatus of claim 3, wherein the counter electrode is configured to substantially span the width of the continuous sheet type substrate as the continuous sheet type substrate passes by the counter electrode during electrodeposition.
5. The apparatus of claim 4, wherein the counter electrode comprises a substantially planar surface that is positioned substantially parallel to the surface of the substrate during electrodeposition.
6. The apparatus of claim 5, wherein the counter electrode and the substrate are between about 2 mm and about 10 mm apart during electrodeposition.
7. The apparatus of claim 6, wherein the flow manifold is configured to produce a substantially laminar flow or a turbulent flow of the electrolyte between the substrate and the counter electrode.
8. The apparatus of claim 7, further comprising one or more seals, said seals configured to channel the flow of electrolyte in order to maximize contact with the substrate and minimize the amount of electrolyte needed to produce the continuous supply of electrolyte contacting the substrate during electrodeposition.
9. The apparatus of claim 8, further comprising one or more overflow channels for collecting used electrolyte.
10. The apparatus of claim 9, wherein the one or more seals are configured to form a chamber between the substrate and the flow manifold when the flow manifold and the substrate are engaged with, or in close proximity to, said one or more seals; said flow manifold further comprising an electrolyte inlet and an electrolyte outlet, each contained within the chamber during electrodeposition.
11. The apparatus of claim 10, wherein the one or more seals comprise a perimeter-type seal.
12. An electrodeposition method comprising:
   (i) flowing an electrolyte between a substrate and a counter electrode using a flow manifold that supplies a continuous supply of electrolyte to the substrate while the plating surface of said substrate is in close proximity to the counter electrode; and
   (ii) applying a plating potential between the substrate and the counter electrode; wherein the counter electrode is configured to substantially span at least one dimension of the substrate and is positioned on, or an integral component of, the flow manifold.
13. The method of claim 12, further comprising moving the substrate continuously past the counter electrode during electrodeposition, wherein the substrate comprises a continuous sheet, said continuous sheet comprising at least one of an electrically conductive material and a material having an electrically conductive coating.
14. The method of claim 13, wherein the counter electrode and the substrate are positioned between about 2 mm and about 10 mm apart during electrodeposition.
15. The method of claim 14, wherein flowing an electrolyte between the substrate and the counter electrode comprises producing a substantially laminar flow or a turbulent flow of the electrolyte between the substrate and the counter electrode.
16. The method of claim 15, further comprising employing one or more seals, said seals configured to channel the flow of electrolyte in order to maximize contact with the substrate and minimize the amount of electrolyte needed to produce the continuous supply of electrolyte contacting the substrate during electrodeposition.
17. The method of claim 16, wherein the one or more seals are configured to form a chamber between the substrate and the flow manifold when the flow manifold and the substrate are engaged with said one or more seals; said flow manifold further comprising an electrolyte inlet configured to supply electrolyte to the chamber and an electrolyte outlet configured to drain used electrolyte from the chamber during electrodeposition.
18. The method of claim 17, wherein the one or more seals comprise a perimeter-type seal.
19. A flow manifold for delivering an electroplating solution to the surface of a substrate, said flow manifold comprising:
   (i) an electrolyte inlet, the electrolyte inlet upstream of;
   (ii) a counter electrode, the counter electrode disposed on a surface of the flow manifold; and
   (iii) an electrolyte outlet, the electrolyte outlet downstream of the counter electrode; wherein the flow manifold is configured to supply a continuous flow of the electroplating solution from the electrolyte inlet, between the counter electrode a surface of the substrate so that electroplating can occur on the surface of the substrate, and then drain via the electrolyte outlet.
20. The flow manifold of claim 19, configured to produce a substantially laminar flow or a turbulent flow of the electroplating solution between the surface of the substrate and the counter electrode.
21. The flow manifold of claim 20, further comprising one or more seals, said seals configured to channel the flow of electroplating solution in order to maximize contact with the surface of the substrate and minimize the amount of plating solution needed to produce the continuous flow of the electroplating solution contacting the substrate during electrodeposition.
22. The flow manifold of claim 21, further comprising one or more overflow channels for collecting used electrolyte.
23. The flow manifold of claim 22, wherein the one or more seals are configured to form a chamber between the surface of the substrate and the flow manifold when the flow manifold and the substrate are engaged with said one or more seals.
24. The flow manifold of claim 23, wherein the one or more seals comprise a perimeter-type seal.