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(54) ROLL-TO-ROLL ELECTROPLATING FOR PHOTOVOLTAIC FILM MANUFACTURING

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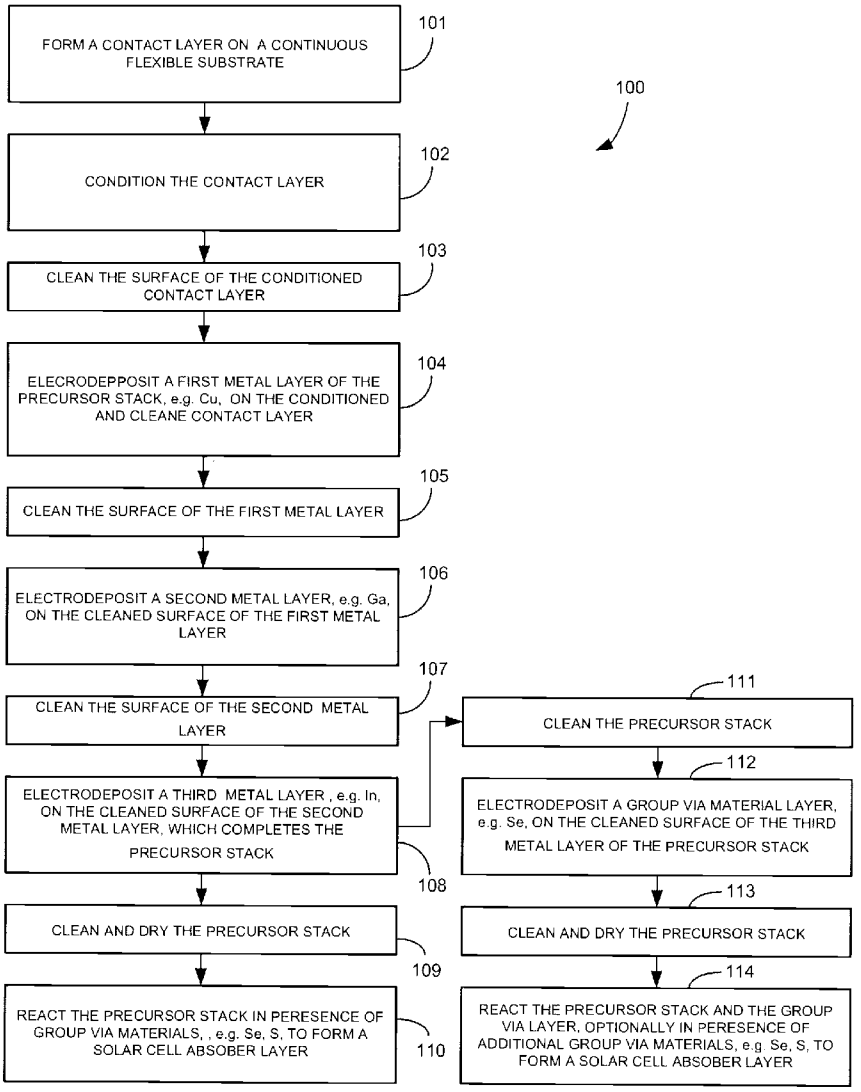
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(57) **ABSTRACT**

A roll to roll system for forming an absorber structure for solar cells on a flexible foil as the flexible foil is advanced through units of the system and by unwrapping from a supply spool and wrapping around a take-up spool. Surface of the flexible foil is first conditioned in a conditioning unit to form an activated surface. A precursor stack including copper, gallium and indium layers is electroplated onto the activated surface by utilizing separate electroplating units for each layers. The precursor layer is reacted with at least one of Se and S in an annealing unit of the system.



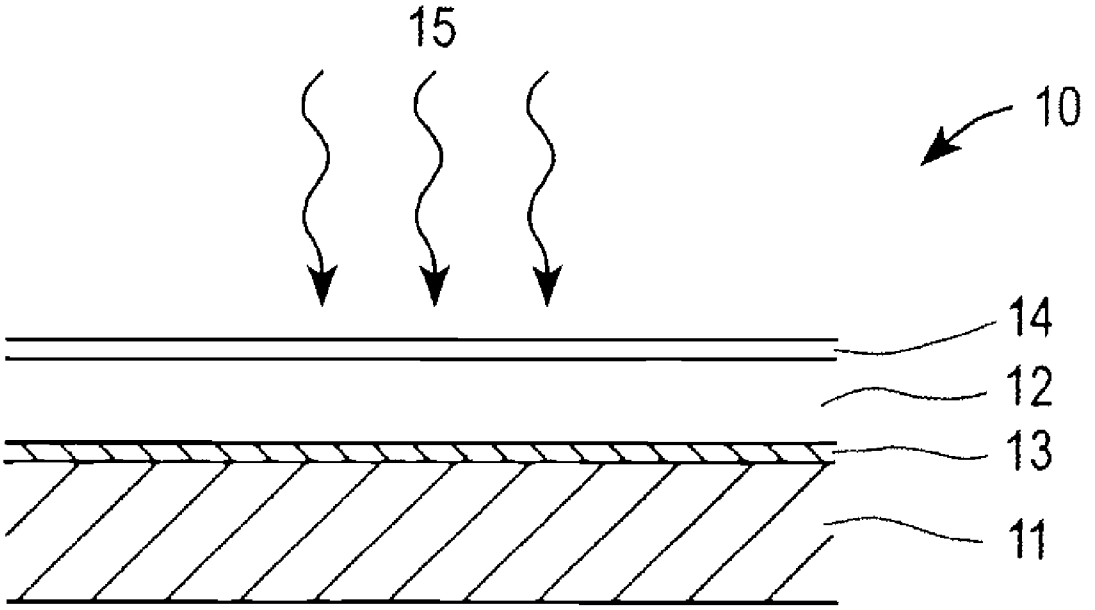


FIG. 1

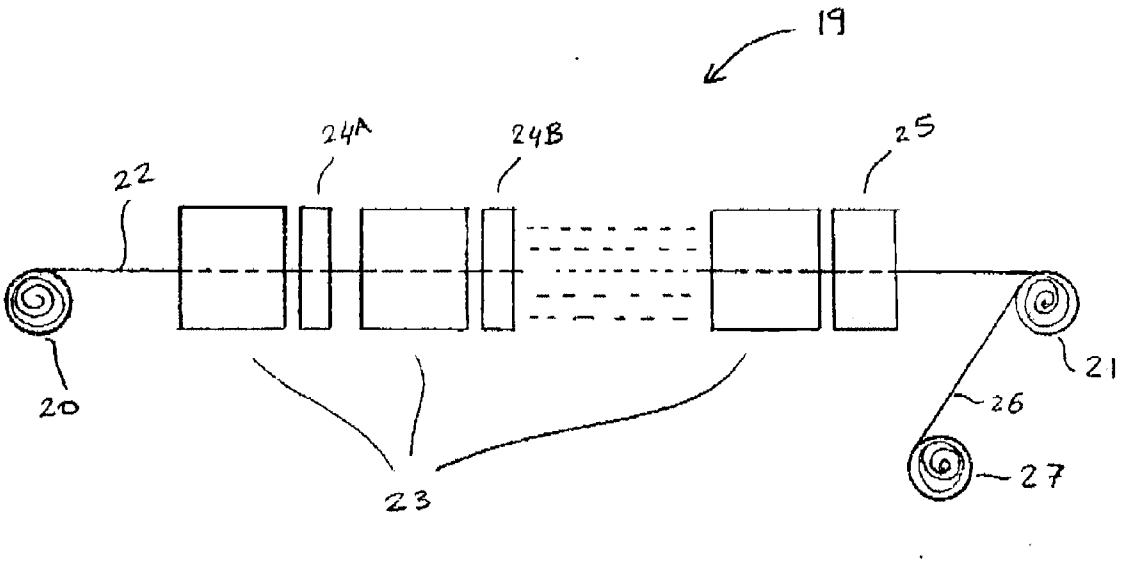


FIG. 2

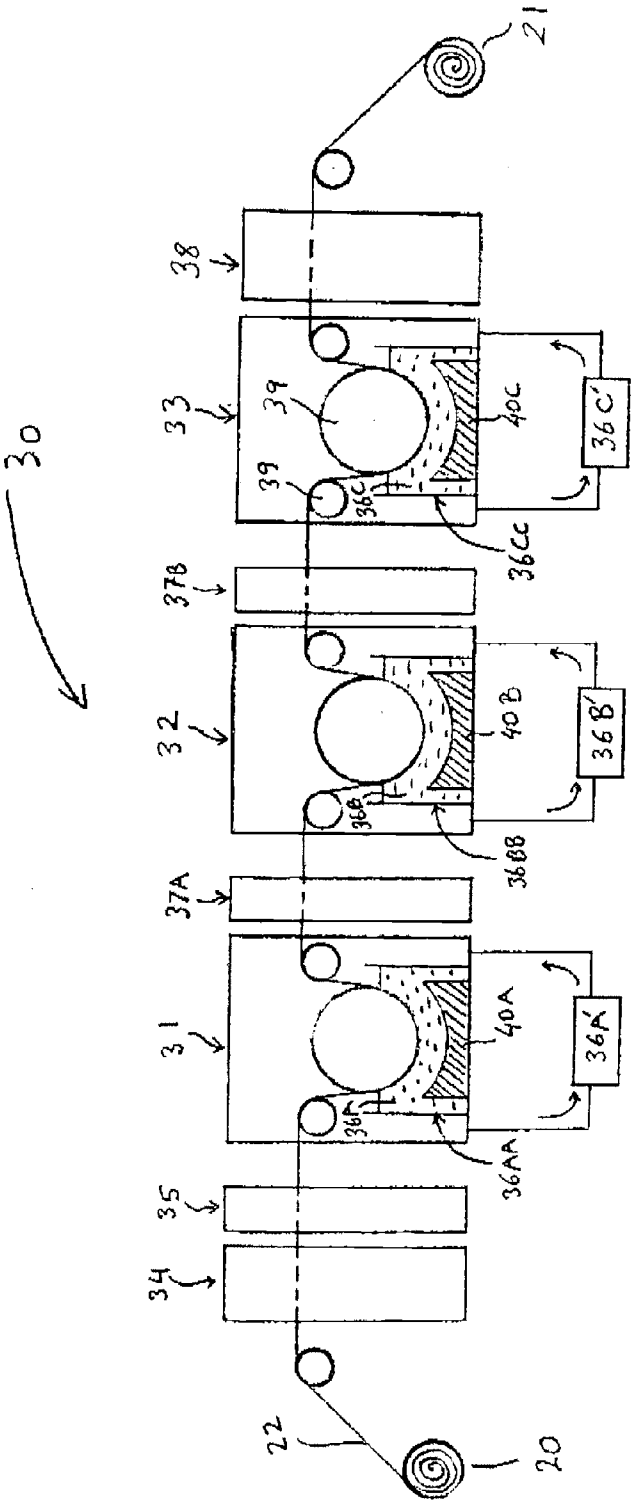

30
21
38
33
39
39
36C
40C
36C'
36Cc
37B
32
40B
36B'
36B
36Bb
37A
31
40A
36A'
36A
36Aa
35
34
22
20

FIG. 3

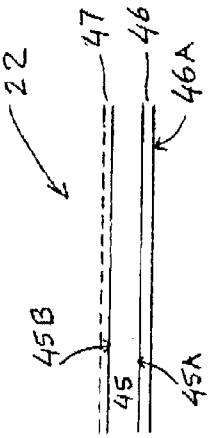

22
47
46
46A
45B
45
45A

FIG. 3A

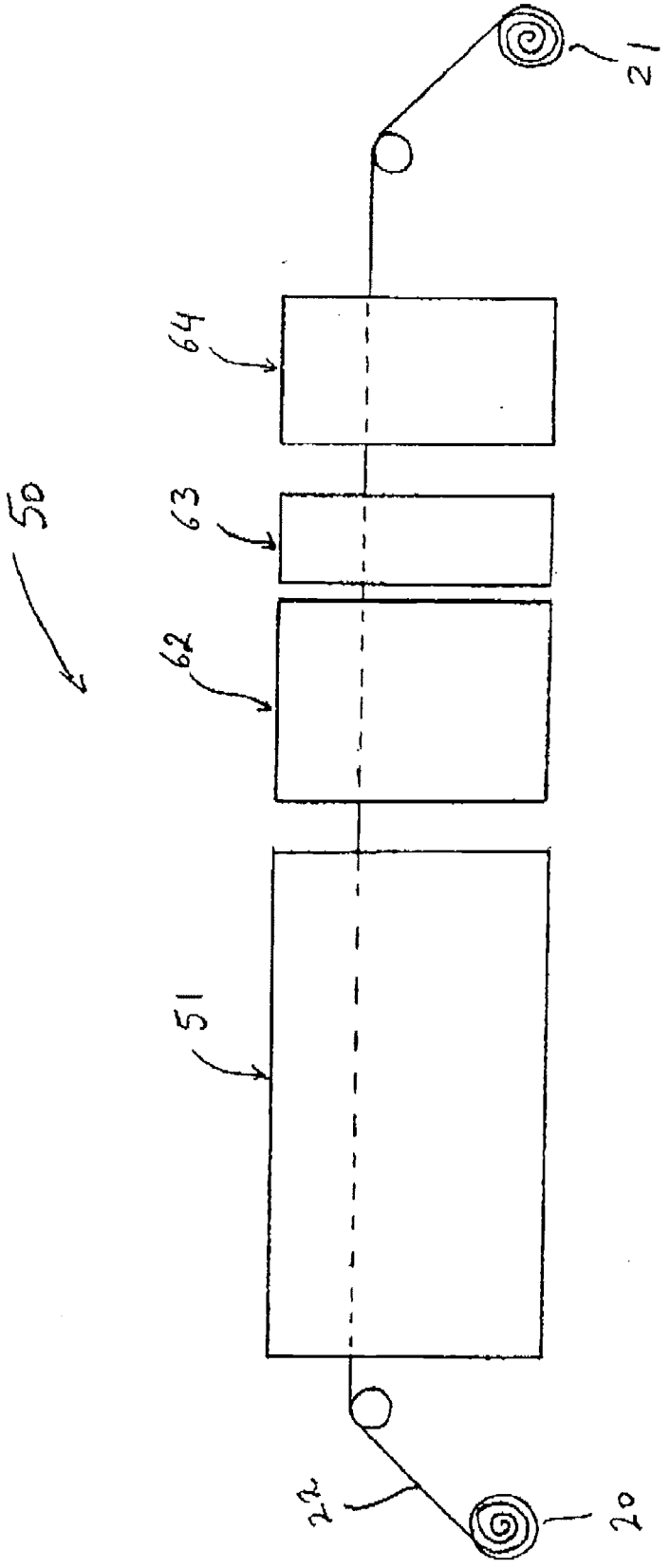


FIG. 4

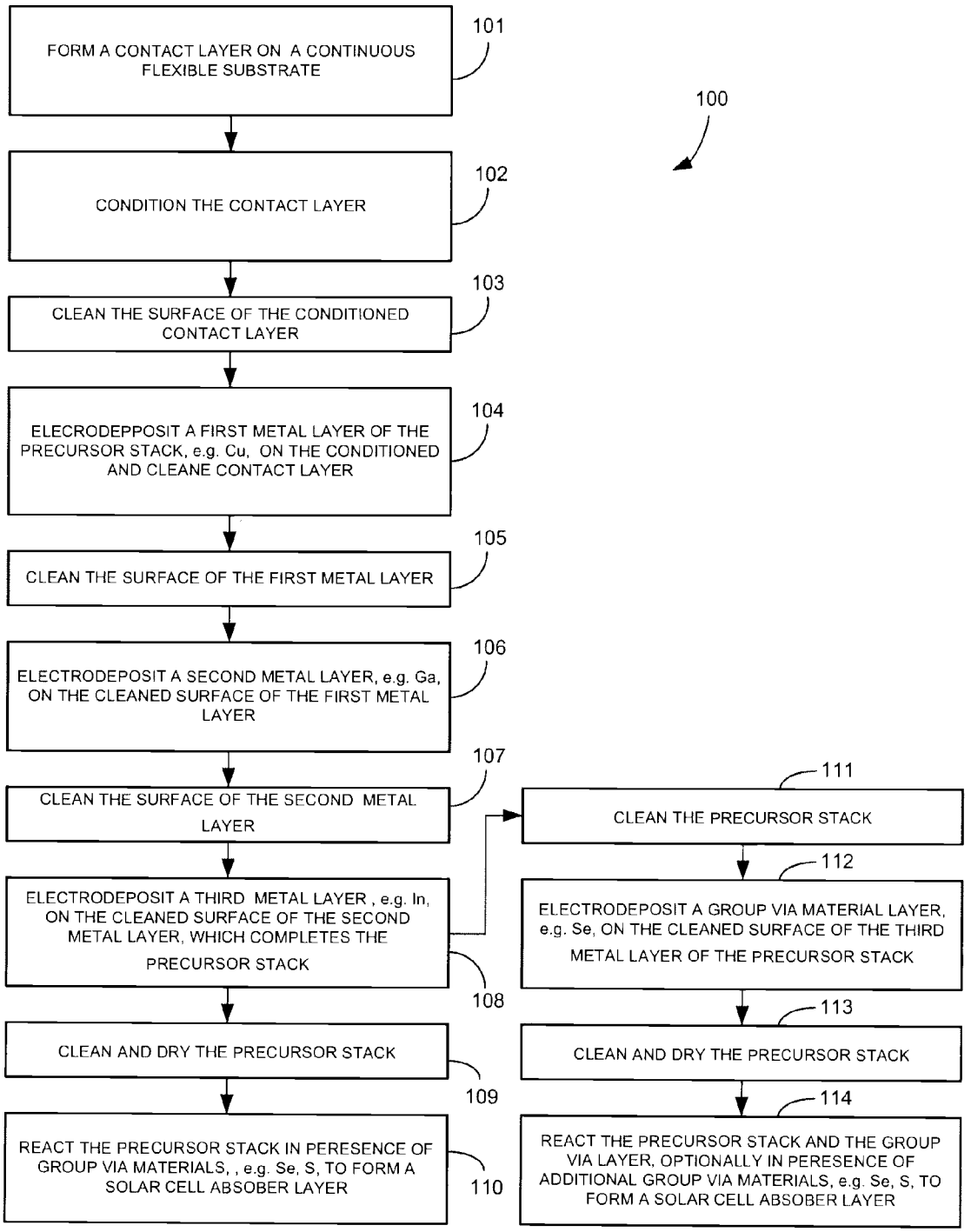

FORM A CONTACT LAYER ON A CONTINUOUS FLEXIBLE SUBSTRATE
101
100
CONDITION THE CONTACT LAYER
102
CLEAN THE SURFACE OF THE CONDITIONED CONTACT LAYER
103
ELECRODEPPOSIT A FIRST METAL LAYER OF THE PRECURSOR STACK, e.g. Cu, ON THE CONDITIONED AND CLEANE CONTACT LAYER
104
CLEAN THE SURFACE OF THE FIRST METAL LAYER
105
ELECTRODEPOSIT A SECOND METAL LAYER, e.g. Ga, ON THE CLEANED SURFACE OF THE FIRST METAL LAYER
106
CLEAN THE SURFACE OF THE SECOND METAL LAYER
107
ELECTRODEPOSIT A THIRD METAL LAYER , e.g. In, ON THE CLEANED SURFACE OF THE SECOND METAL LAYER, WHICH COMPLETES THE PRECURSOR STACK
108
CLEAN AND DRY THE PRECURSOR STACK
109
REACT THE PRECURSOR STACK IN PERESENCE OF GROUP VIA MATERIALS, , e.g. Se, S, TO FORM A SOLAR CELL ABSOBER LAYER
110
111
CLEAN THE PRECURSOR STACK
112
ELECTRODEPOSIT A GROUP VIA MATERIAL LAYER, e.g. Se, ON THE CLEANED SURFACE OF THE THIRD METAL LAYER OF THE PRECURSOR STACK
113
CLEAN AND DRY THE PRECURSOR STACK
114
REACT THE PRECURSOR STACK AND THE GROUP VIA LAYER, OPTIONALLY IN PERESENCE OF ADDITIONAL GROUP VIA MATERIALS, e.g. Se, S, TO FORM A SOLAR CELL ABSOBER LAYER

Figure 5

ROLL-TO-ROLL ELECTROPLATING FOR PHOTOVOLTAIC FILM MANUFACTURING

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to Provisional Application Ser. No. 60/862,164 filed on Oct. 19, 2006.

FIELD OF THE INVENTION

[0002] The present invention relates to methods and apparatus for preparing thin films of Group IBIIIAVIA compound semiconductor films for radiation detector and photovoltaic applications.

BACKGROUND

[0003] Solar cells are photovoltaic devices that convert sunlight directly into electrical power. The most common solar cell material is silicon, which is in the form of single or polycrystalline wafers. However, the cost of electricity generated using silicon-based solar cells is higher than the cost of electricity generated by the more traditional methods. Therefore, since early 1970's there has been an effort to reduce cost of solar cells for terrestrial use. One way of reducing the cost of solar cells is to develop low-cost thin film growth techniques that can deposit solar-cell-quality absorber materials on large area substrates and to fabricate these devices using high-throughput, low-cost methods.

[0004] Group IBIIIAVIA compound semiconductors comprising some of the Group IB (Cu, Ag, Au), Group IIIA (B, Al, Ga, In, Tl) and Group VIA (O, S, Se, Te, Po) materials or elements of the periodic table are excellent absorber materials for thin film solar cell structures. Especially, compounds of Cu, In, Ga, Se and S which are generally referred to as CIGS(S), or $Cu(In,Ga)(S,Se)_2$ or $CuIn_{1-x}Ga_x(S_ySe_{1-y})_k$, where $0 \leqq x \leqq 1$, $0 \leqq y \leqq 1$ and k is approximately 2, have already been employed in solar cell structures that yielded conversion efficiencies approaching 20%. Absorbers containing Group IIIA element Al and/or Group VIA element Te also showed promise. Therefore, in summary, compounds containing: i) Cu from Group IB, ii) at least one of In, Ga, and Al from Group IIIA, and iii) at least one of S, Se, and Te from Group VIA, are of great interest for solar cell applications.

[0005] The structure of a conventional Group IBIIIAVIA compound photovoltaic cell such as a $Cu(In,Ga,Al)(S,Se,Te)_2$ thin film solar cell is shown in FIG. **1**. The device **10** is fabricated on a substrate **11**, such as a sheet of glass, a sheet of metal (such as aluminum or stainless steel), an insulating foil or web, or a conductive foil or web. The absorber film **12**, which comprises a material in the family of $Cu(In,Ga,Al)(S,Se,Te)_2$, is grown over a conductive layer **13**, which is previously deposited on the substrate **11** and which acts as the electrical contact to the device. Various conductive layers comprising Mo, Ta, W, Ti, and stainless steel etc. have been used in the solar cell structure of FIG. **1**. If the substrate itself is a properly selected conductive material, it is possible not to use a conductive layer **13**, since the substrate **11** may then be used as the ohmic contact to the device. After the absorber film **12** is grown, a transparent layer **14** such as a CdS, ZnO or CdS/ZnO stack is formed on the absorber film. Radiation **15** enters the device through the transparent layer **14**. Metallic grids (not shown) may also be deposited over the transparent layer **14** to reduce the effective series resistance of the device. It should be noted that the structure of FIG. **1** may also be inverted if substrate is transparent. In that case light enters the device from the substrate side of the solar cell.

[0006] In a thin film solar cell employing a Group IBIIIAVIA compound absorber, the cell efficiency is a strong function of the molar ratio of IB/IIIA. If there are more than one Group IIIA materials in the composition, the relative amounts or molar ratios of these IIIA elements also affect the properties. For a $Cu(In,Ga)(S,Se)_2$ absorber layer, for example, the efficiency of the device is a function of the molar ratio of Cu/(In+Ga). Furthermore, some of the important parameters of the cell, such as its open circuit voltage, short circuit current and fill factor vary with the molar ratio of the IIIA elements, i.e. the Ga/(Ga+In) molar ratio. In general, for good device performance Cu/(In+Ga) molar ratio is kept at around or below 10.0. As the Ga/(Ga+In) molar ratio increases, on the other hand, the optical bandgap of the absorber layer increases and therefore the open circuit voltage of the solar cell increases while the short circuit current typically may decrease. It is important for a thin film deposition process to have the capability of controlling both the molar ratio of IB/IIIA, and the molar ratios of the Group IIIA components in the composition. It should be noted that although the chemical formula is often written as $Cu(In,Ga)(S,Se)_2$, a more accurate formula for the compound is $Cu(In,Ga)(S,Se)_k$, where k is typically close to 2 but may not be exactly 2. For simplicity we will continue to use the value of k as 2. It should be further noted that the notation "Cu(X,Y)" in the chemical formula means all chemical compositions of X and Y from (X=0% and Y=100%) to (X=100% and Y=0%). For example, Cu(In,Ga) means all compositions from CuIn to CuGa. Similarly, $Cu(In,Ga)(S,Se)_2$ means the whole family of compounds with Ga/(Ga+In) molar ratio varying from 0 to 1, and Se/(Se+S) molar ratio varying from 0 to 1.

[0007] The first technique used to grow $Cu(In,Ga)Se_2$ layers was the co-evaporation approach which involves evaporation of Cu, In, Ga and Se from separate evaporation boats onto a heated substrate, as the deposition rate of each component is carefully monitored and controlled.

[0008] Another technique for growing $Cu(In,Ga)(S,Se)_2$ type compound thin films for solar cell applications is a two-stage process where at least two of the components of the $Cu(In,Ga)(S,Se)_2$ material are first deposited onto a substrate, and then reacted with S and/or Se in a high temperature annealing process. For example, for $CuInSe_2$ growth, thin sub-layers of Cu and In are first deposited on a substrate to form a precursor layer and then this stacked precursor layer is reacted with Se at elevated temperature. If the reaction atmosphere contains sulfur, then a $CuIn(S,Se)_2$ layer can be grown. Addition of Ga in the precursor layer, i.e. use of a Cu/In/Ga stacked film precursor, allows the growth of a $Cu(In,Ga)(S,Se)_2$ absorber. Other prior-art techniques include deposition of Cu—Se/In—Se, Cu—Se/Ga—Se, or Cu—Se/In—Se/Ga—Se stacks and their reaction to form the compound. Mixed precursor stacks comprising compound and elemental sub-layers, such as a Cu/In—Se stack or a Cu/In—Se/Ga—Se stack, have also been used, where In—Se and Ga—Se represent selenides of In and Ga, respectively.

[0009] Sputtering and evaporation techniques have been used in prior art approaches to deposit the sub-layers containing the Group IB and Group IIIA components of metallic precursor stacks. In the case of $CuInSe_2$ growth, for example, Cu and In sub-layers were sequentially sputter-deposited from Cu and In targets on a substrate and then the stacked precursor film thus obtained was heated in the presence of gas containing Se at elevated temperatures as described in U.S. Pat. No. 4,798,660. More recently U.S. Pat. No. 6,048,442 disclosed a method comprising sputter-depositing a stacked precursor film comprising a Cu—Ga alloy sub-layer and an In sub-layer to form a Cu—Ga/In stack on a metallic back electrode and then reacting this precursor stack film with one of Se and S to form the compound absorber layer. U.S. Pat. No. 6,092,669 described sputtering-based equipment and method for producing such absorber layers.

[0010] One prior art method described in U.S. Pat. No. 4,581,108 utilizes an electrodeposition approach for metallic precursor preparation. In this method a Cu sub-layer is first electrodeposited on a substrate. This is then followed by electrodeposition of an In sub-layer and heating of the deposited Cu/In precursor stack in a reactive atmosphere containing Se. This technique was found to require very high plating current densities resulting in non-uniformities and problems of adhesion to the substrate as discussed in reference publications (Kapur et al., "Low Cost Thin Film Chalcopyrite Solar Cells, Proceedings of 18th IEEE Photovoltaic Specialists Conf., 1985, p. 1429; "Low Cost Methods for the Production of Semiconductor Films for CIS/CdS Solar Cells", Solar Cells, vol. 21, p. 65, 1987).

[0011] As the brief review above demonstrates there is still a need to develop high-throughput, low cost techniques to manufacture thin film solar cells and modules.

SUMMARY OF THE INVENTION

[0012] The present invention provides a roll to roll system to form solar cell absorbers by continuously processing a surface of a flexible foil as the flexible foil is advanced through processing units of the roll to roll system.

[0013] An aspect of the present invention provides a system for forming an absorber structure for solar cells on a front surface of a continuous flexible workpiece as the continuous flexible workpiece is advanced through units of the system. The system includes a conditioning unit to condition the front surface of the continuous flexible workpiece to form activated surface portions.

[0014] The system further includes a first electroplating unit to form a first layer of a precursor stack by electroplating a metal belonging to one of Group IB and Group IIIA of the periodic table on an activated surface portion of the continuous flexible workpiece as the continuous flexible workpiece is advanced through the first electroplating station. A first cleaning unit of the system is to clean the first layer deposited in the first electroplating unit.

[0015] The system further includes a second electroplating unit to form a second layer of the precursor stack by electroplating a metal belonging to one of Group IB and Group IIIA of the periodic table onto the first layer as the continuous flexible foil is advanced through the first and the second electroplating units and while the first layer is continued to be electroplated onto a following activated surface portion of the surface of the continuous flexible foil in the first electroplating unit. The first layer is different from the second layer. A second cleaning unit of the system is to clean the second layer deposited in the second electroplating unit.

[0016] The system further includes a third electroplating unit to form a third layer by electroplating a metal belonging to one of Group IB and Group IIIA of the periodic table onto the second layer to complete the precursor stack as the flexible foil is advanced through the first, second and third electroplating stations and while the second layer is continued to be electroplated in the second electroplating station on the first layer that is electroplated on the following activated portion of the surface of the flexible foil, and while the first layer is continued to be electroplated onto another following activated portion of the surface of the flexible foil in the first electroplating station. The third layer is different from the first and second layers. The system further includes a moving assembly to hold and linearly move the continuous flexible workpiece through the units of the system, wherein the moving assembly comprises a feed spool to unwrap and feed unprocessed portions of the continuous flexible workpiece into the system and a take-up spool to receive the processed portions and wrap them around.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] FIG. **1** is a cross-sectional view of a solar cell employing a Group IBIIIAVIA absorber layer.

[0018] FIG. **2** shows a roll to roll electrodeposition system of the present invention.

[0019] FIG. **3** shows another roll to roll electrodeposition system of the present invention comprising multiple electroplating units and cleaning units.

[0020] FIG. **3**A shows a structure of the flexible foil base.

[0021] FIG. **4** shows a roll to roll processing system comprising additional processing units including a Group VIA material electroplating unit.

[0022] FIG. **5** shows a flow chart of an embodiment of a process using roll to roll system

DETAILED DESCRIPTION

[0023] Present invention provides a low-cost, high throughput two-stage process for fabrication of CIGS(S) type absorber layers for manufacturing of solar cells.

[0024] FIG. **2** schematically shows an embodiment of the process and the tool of the present invention. In this embodiment, a roll-to-roll processing technique is used to electrodeposit a Group IB material (preferably Cu) and a Group IIIA material (preferably at least one of In and Ga) in a continuous manner on a continuous flexible workpiece **22** such as a flexible foil base including a flexible substrate and a contact layer. The tool **19** has a supply spool **20** and a return spool **21** and the flexible foil base **22** is directed from the supply spool **20** to the return spool **21** through a series of electroplating units **23**. The process units **23** may include at least one Group IB material electroplating unit, and at least one Group IIIA material electroplating unit. After each electroplating unit **23**, there may preferably be cleaning units **24**A, **24**B. The cleaning units rinse the electroplated

surface after each electroplating process, and thus avoid cross contamination of the electroplating electrolytes or baths in the electroplating units **23**. For example, after a section of the base **22** is electroplated or electrocoated with Cu in an electroplating unit, the section passes through a cleaning unit where the chemical residues of the Cu plating bath on the section are rinsed off and the section moves into a Group IIIA electroplating unit such as a Ga electroplating unit. It should be noted that the section may also be dried after the rinsing step; however, in general it is preferable to keep the surface of the already plated material layer wet as it goes into another electroplating bath. There is a need to provide a rinse/dry unit **25** at the end of the tool **19** to assure that the flexible foil base **22** comprising electroplated Group IB and Group IIIA materials is completely clean and dry before being rolled onto the return spool **21**. To avoid damage to the electroplated layers, a packing sheet **26** may be fed from a packing spool **27**, to between the layers of the flexible foil base **22** comprising the electroplated Group IB and Group IIIA materials on the return spool **21**. The packing sheet **26** may be a paper or thin polymeric sheet.

[**0025**] Flow chart **100** shown in FIG. **5** provides an exemplary process flow for an embodiment of the roll to roll system of the present invention. Initially, as shown in box **101**, a contact layer may be formed on the continuous flexible substrate to form a continuous flexible workpiece on which a precursor stack of the present invention would be built using the system of this invention. Next, as shown in box **102**, in a surface activation step, surface of the contact layer is conditioned to form an activated surface for the following electrodeposition process. As shown in box **103**, the surface of the conditioned contact layer may be cleaned, e.g., rinsed with a cleaning solution before an electrodeposition process to remove possible chemical residues and particles from the surface of the contact layer.

[**0026**] It should be noted that the surface activation step is very important because electrodeposition efficiency on a surface depends on the nature of that surface on which a material is deposited. An activated surface is a material surface that is electrochemically active and can be electroplated with efficiency. If the surface is electrochemically passive, electrodeposition efficiency is generally low and adhesion is poor. However, on an active, or activated, surface electrodeposition efficiency is higher and more consistent. Consistent electrodeposition efficiency yields consistent thickness for the electrodeposited material. In the present invention CIGS type absorber layers are formed employing precursor stacks such as Cu/Ga/In or Cu/Ga/Cu/In stacks. The thicknesses of the layers within the stack need to be tightly controlled to be able to control the Cu/(In+Ga) and Ga/(In+Ga) molar ratios which are typically below 1 and which are important for the quality of the resulting absorbers and the performance of solar cells fabricated on such absorbers. A typical target ratio for Cu/(In+Ga) may be in the range of 0.8-0.95. In a roll-to-roll system the contact layer on which a first layer such as a Cu layer would be deposited may be exposed to the atmosphere for different periods of time depending on the location on the roll. For example, in a roll that may be 5000 ft long, the contact layer at the beginning of the roll may be coated with Cu within a few minutes whereas a portion of the contact layer at the end of the roll may be coated after 41 hours if the continuous flexible workpiece moves at a rate of 2 ft/minute. Such variation in exposure of the contact layer to atmosphere may induce differences in the condition of the contact layer surface due to oxidation, exposure to chemical fumes etc. Plating efficiency of the Cu layer on the contact layer may then be different on portions of the contact layer at the beginning of the roll and at the end of the roll. Such differences in efficiency, in turn, cause differences in the thickness of the Cu layer throughout the flexible workpiece and thus cause a change in the Cu/(In+Ga) molar ratio. As a result, process yields are reduced, and manufacturability of high efficiency solar cells at high yields cannot be achieved. By employing an activation chamber and activation process step before the electrodeposition of the first layer on the contact layer, consistence of electrodeposition efficiency of the first layer on the contact layer is assured throughout the roll and yield for consistent Cu/(In+Ga) ratio is assured.

[**0027**] Conditioning process of the present invention results in an electroplating efficiency of more than 90% when a subsequent electroplating process is performed and the first metal layer such as a copper layer is electroplated onto the activated surface. For example, an activated surface formed on the contact layer by a cathodic conditioning process provides more than 90% electroplating efficiency for the subsequent electroplating process, such as copper electroplating. However, if the surface is electrochemically passive, the electroplating efficiency is low, less than 90%, maybe even as low as 20-50%.

[**0028**] Boxes **104** through **108** show a process sequence to form a precursor stack of the present invention. As shown in box **104**, in a first electrodeposition step, a Group IB material such as copper, may be electrodeposited on the conditioned and cleaned surface of the contact layer. This step is followed by a cleaning step to clean the surface of the electrodeposited Group IB material, box **105**. As shown in box **106**, in a second electrodeposition step, a first Group IIIA material, such as gallium, may be electrodeposited on the surface of the cleaned Group IB material layer. This step is followed by a cleaning step to clean the surface of the electrodeposited first Group IIIA material layer, box **107**. As shown in box **108**, in a third electrodeposition step, a second Group IIIA material, such as indium, may be electrodeposited on the surface of the cleaned first Group IIIA material layer, which completes the precursor stack. The precursor stack may be cleaned and dried following step, box **109**. The precursor stack may be reacted in presence of Group VIA materials, such as selenium and sulfur with gas phase delivery, to form an absorber, box **10**.

[**0029**] Alternately, the precursor layer in box **108** may be just cleaned without drying, as shown in box **111**, to electrodeposit a Group VIA material onto the precursor stack as shown in box **112**. Following the electrodeposition process, the precursor stack with the Group VIA layer is cleaned, box **113**, and reacted to form an absorber, box **114**. During the reaction, optionally, additional Group VIA materials may be introduced to the forming absorber.

[**0030**] The roll-to-roll processing approach of the present invention offers several advantages. Electrodeposition is a surface sensitive process. Defects in electrodeposited layers mostly originate from the surface they are plated on. Therefore, it is preferable to minimize handling of substrates in an electroplating approach. Surfaces to be plated need to be protected from physical contact, particles etc. that may later cause defectivity in the films deposited on such surfaces.

Plating efficiency and the thickness uniformity of electroplated layers are also affected by the condition of the surface they are plated on. For example, electrodeposition of Cu, Ga or In on a chemically active, fresh surface is a much more repeatable process compared to electrodeposition on a surface that may be exposed to air, chemical vapors or, in general, to outside environment for varying amounts of time. In a roll-to-roll process all depositions are done in a controlled environment (enclosure for the roll not shown in figures) and the time between depositions are minimized unlike a batch process that requires several loading and unloading steps to deposit a stack of materials on a base. In the present roll-to-roll process a material, such as Cu is plated on a section of the base. The surface of this plated material is fresh and active after plating and after the water rinse step. Therefore, when section moves into the next plating bath, for example a Ga or In plating bath, within a few seconds or minutes, deposition initiates on this active surface. If the velocity of the foil base is constant, then the Ga or In plating always operates on the same Cu surface in terms of activity. This provides highly repeatable results in terms of thickness and uniformity of the In and Ga layers. Same is true for the Cu layer also.

[0031] If the Cu layer is first to be deposited on the flexible foil base, the surface of the flexible foil base may first be activated by passing it through a pre-deposition electrolyte and applying a pre-deposition process step or conditioning to the surface. The predeposition process step may be an etching step or an electrotreating step such as a cathodic conditioning step comprising applying a cathodic voltage to the base with respect to an electrode in the pre-deposition electrolyte or an anodic conditioning step comprising applying an anodic voltage to the base with respect to an electrode in the pre-deposition electrolyte. Conditioning step may also include a pickling step; or a deposition step comprising depositing a fresh layer on the base before the deposition of Cu. In all such cases, an active surface may be provided to the Cu electrodeposition step so that this step yields repeatable results in terms of Cu layer thickness and uniformity. As described before, thickness and uniformity control for deposited Cu, In and/or Ga layers are of utmost importance since Cu/(In+Ga) and Ga/(In+Ga) molar ratios need to be controlled throughout the base.

[0032] FIG. **3** shows an exemplary roll-to-roll electroplating system **30** with capability to produce, on a flexible foil base **22**, metallic stacks comprising Cu, In and Ga with excellent thickness control and uniformity. The electroplating system **30** comprises a series of process units, a supply spool **20**, a return spool **21** and a mechanism (not shown) to direct the flexible foil base **22** from the supply spool **20** to the return spool **21** through the series of process units. The series of process units comprises at least one Cu electroplating unit **31**, at least one Ga electroplating unit **32**, and at least one In electroplating unit **33**. It should be noted that the order of these electroplating units may be changed to obtain various stacks on the base. For example, the order of the electroplating units shown in FIG. **3** would yield a stack of Cu/Ga/In on the base. Changing this order and optionally adding other electroplating units one may obtain stacks such as Cu/In/Ga, In/Cu/Ga, Ga/Cu/In, Cu/Ga/Cu/In, Cu/Ga/Cu/In/Cu, Cu/In/Cu/Ga, Cu/In/Cu/Ga/Cu etc. It should be noted that many more iterations of such stacks are possible. However, stacks initiating with a Cu layer are preferred because Cu plating yields highly controlled, good morphology coatings at high plating efficiency, and Cu is a good base on which Ga and/or In films can be electroplated. In the following, the present invention will be described using the configuration in FIG. **3** with the electroplating system **30** comprising one of each of a Cu electroplating unit, a Ga electroplating unit and an In electroplating unit.

[0033] In the electroplating system **30** of FIG. **3** there is, preferably, a conditioning unit **34** that conditions the surface of the flexible foil base **22** on which a Cu layer will be deposited in the Cu electroplating unit **31**. A typical structure of the flexible foil base **22** is shown in FIG. **3**A. The flexible foil base **22** comprises a flexible foil substrate **45** and a conductive layer **46** or a contact layer deposited on a first surface **45**A of the flexible foil substrate **45**. The flexible foil substrate **45** may be made of any polymeric or metallic foil, but preferably it is a metallic foil such as a 20-250 um thick stainless steel foil, Ti foil, Al foil or aluminum alloy foil. Various metallic foil substrates (such as Cu, Ti, Mo, Ni, Al) have previously been identified for CIGS(S) solar cell applications (see for example, B. M. Basol et al., "Status of flexible CIS research at ISET", NASA Document ID: 19950014096, accession No: 95N-20512, available from NASA Center for AeroSpace Information). The conductive layer **46** may be in the form of a single layer or alternately it may comprise a stack of various sublayers (not shown). Preferably, the conductive layer comprises at least one diffusion barrier layer that prevents diffusion of impurities from the flexible foil substrate **45** into the layers to be electrodeposited and into the CIGS(S) layer during its formation. Materials of the conductive layer **46** include but are not limited to Ti, Mo, Cr, Ta, W, Ru, Ir, Os, and nitrides and oxy-nitrides of these materials. Preferably, the free surface **46**A of the conductive layer **46** comprises at least one of Ru, Ir and Os for better nucleation of the electroplated layers.

[0034] In this example, electrodeposition is carried out on the free surface **46**A of the conductive layer **46**. The back surface **45**B of the flexible foil substrate **45** may optionally be covered with a secondary layer **47** (shown with dotted line) to protect the flexible foil substrate **45** during annealing/reaction steps that will follow to form the CIGS(S) compound, or to avoid buckling of the flexible foil substrate **45**. It is important that the material of the secondary layer **47** be stable in chemistries of the Cu, In and Ga plating baths, i.e. not dissolve into and contaminate such baths, and also be resistant to reaction with Group VIA elements. Materials that can be used in the secondary layer **47** include but are not limited to Ru, Os, Ir, Ta, W etc. Use of a secondary layer **47** comprising at least one of Ru, Ir and Os has an added benefit. Such materials are very resistant to reaction with Se, S and Te. Therefore, after any reaction step that forms CIGS(S) compound layer on the free surface **46**A of the conductive layer **46**, the secondary layer protects the flexible foil substrate **45** from reaction with Se, S or Te and leaves a surface that can be soldered easily. In prior art devices Mo was used as the secondary layer **47**. During selenization and/or sulfidation processes or during the growth of the CIGS(S) absorber, this Mo layer reacted with Se and/or S forming a Mo(S,Se) surface layer. After solar cells are completed, they need to be interconnected to form modules. Interconnection involves soldering or otherwise attaching back surface of each cell to the front surface of the adjacent cell. A Mo(S,Se) layer on the back of the cell cannot be soldered effectively, therefore physical removal of the sele-

nized and/or sulfidized Mo surface is needed. However, a surface comprising at least one of Ru, Ir and Os can be soldered easily without the added step of removing a selenized or sulfidized surface layer because these materials do not appreciably selenize or sulfidize.

[0035] Referring back to FIG. **3**, the flexible foil base **22** passes through a conditioning unit **34**, and an optional cleaning unit **35**, before entering into the Cu electroplating unit **31**. In the conditioning unit **34**, the surface of the flexible foil base **22** (such as the free surface **46**A of the conductive layer **46** in FIG. **3**A) is conditioned to render it ready for electrodeposition with Cu. Such conditioning may involve exposing the free surface **46**A to an acidic or basic solution for etching and/or activation, applying a cathodic or anodic voltage to the free surface **46**A with respect to an electrode while both the electrode and the free surface **46**A are exposed to an electrolyte, electrodepositing a seed layer on the free surface **46**A, or simply rinsing and wetting the free surface **46**A before it moves into the Cu electroplating unit **31**. If only a rinsing process is carried out in the conditioning unit **34**, there would not be a need to the cleaning unit **35**. Otherwise cleaning unit **35** is needed to remove any residual chemicals left on both faces of the flexible foil base **22** before it moves into the Cu electroplating unit **31**. In the present invention, if a seed layer is electrodeposited on the free surface **46**A in the conditioning unit **34**, this seed layer may be a Cu layer that is 2-50 nm thick and it may be deposited from a bath that yields defect free uniform layers. Complexed Cu electrolytes with high pH are especially suitable for this purpose. Use of seed layers and various chemistries for electroplating are disclosed in Applicant's co-pending U.S. application Ser. No. 11/266,013 filed Nov. 2, 2005 entitled "Technique and Apparatus for Depositing Layers of Semiconductors For Solar Cell and Modular Fabrication", and U.S. application Ser. No. 11/462,685 filed Aug. 4, 2004 entitled "Technique for Preparing Precursor Films and Compound Layers for Thin Film Solar Cell Fabrication and Apparatus Corresponding Thereto", entire contents of these applications are incorporated herein by reference.

[0036] Once a section of the free surface **46**A of the conductive layer **46** is conditioned and cleaned it moves into the Cu electroplating unit **31**. Within the Cu electroplating unit **31**, the free surface **46**A (or the surface of the seed layer if a seed layer has been deposited in the conditioning unit **34**) is exposed to a Cu plating bath **36**A which may be circulated between a first reservoir **36**AA and a first chemical cabinet **36**A'. The Cu plating bath **36**A may be filtered and replenished during circulation or while in the first chemical cabinet **36**A'. Measurement and control of various bath parameters, such as additive content, Cu content, temperature, pH etc. may be continuously or periodically carried out within the first chemical cabinet **36**A' to assure stability of the Cu deposition process. Electrical connection to the conductive layer **46** (or to the flexible foil substrate **45** if the foil substrate itself is conductive) may be achieved by various means including through rollers **39** which may be touching the flexible foil base **22** at, at least part of its back or front surfaces. Preferably, front surface contacts are made at the two edges avoiding physical contact with most of the front surface which may be damaged or contaminated by contacts. A first anode **40**A is placed in the Cu plating bath **36**A and a potential difference is applied between the first anode **40**A and the portion of the conductive layer **46** within the Cu electroplating unit **31**, to deposit Cu on the portion of the free surface **46**A that is exposed to the Cu plating bath **36**A as the flexible foil base **22** is moved.

[0037] The portion of the flexible foil base **22** processed in the Cu electroplating unit **31**, passes through the Cu cleaning unit **37**A and enters into the Ga electroplating unit **32**. Within the Ga electroplating unit, the surface of the already deposited Cu layer is exposed to a Ga plating bath **36**B which may be circulated between a second reservoir **36**BB and a second chemical cabinet **36**B'. The Ga plating bath **36**B may be filtered and replenished during circulation or while in the second chemical cabinet **36**B'. Measurement and control of various bath parameters, such as additive content, Ga content, temperature, pH etc. may be continuously or periodically carried out within the second chemical cabinet **36**B' to assure stability of the Ga deposition process. Electrical connection to the conductive layer **46** (or to the flexible foil substrate **45** if the flexible foil substrate itself is conductive) may be achieved by various means including through rollers **39** which may be touching the base at, at least part of its back or front surfaces. Preferably, front surface contacts are made at the two edges avoiding physical contact with most of the front surface which may be damaged or contaminated by contacts. A second anode **40**B is placed in the Ga plating bath **36**B and a potential difference is applied between the second anode **40**B and the portion of the conductive layer **46** within the Ga electroplating unit **32**, to deposit Ga on the portion of the Cu surface that is exposed to the Ga plating bath **36**B as the flexible foil base **22** is moved.

[0038] The portion of the flexible foil base processed in the Ga electroplating unit **32**, passes through the Ga cleaning unit **37**B and enters into the In electroplating unit **33**. Within the In electroplating unit, the surface of the already deposited Ga layer is exposed to an In plating bath **36**C which may be circulated between a third reservoir **36**CC and a third chemical cabinet **36**C'. The In plating bath **36**C may be filtered and replenished during circulation or while in the third chemical cabinet **36**C'. Measurement and control of various bath parameters, such as additive content, In content, temperature, pH etc. may be continuously or periodically carried out within the third chemical cabinet **36**C' to assure stability of the In deposition process. Electrical connection to the conductive layer **46** (or to the flexible foil substrate **45** if the flexible foil substrate itself is conductive) may be achieved by various means including through rollers **39** which may be touching the flexible foil base at, at least part of its back or front surfaces. Preferably, front surface contacts are made at the two edges avoiding physical contact with most of the front surface which may be damaged or contaminated by contacts. A third anode **40**C is placed in the In plating bath **36**C and a potential difference is applied between the third anode **40**C and the portion of the conductive layer **46** within the In electroplating unit **33**, to deposit In on the portion of the Ga surface that is exposed to the In plating bath **36**C as the base **22** is moved. After In electrodeposition the portion of the flexible foil base comprising the all-electroplated Cu/Ga/In stack is passed through a cleaning/drying unit **38** and moved to the return spool **21**.

[0039] It should be noted that additional process units may be added to the electroplating system **30** of FIG. **3**. For example, another Cu electroplating unit and another cleaning unit may be inserted between the Ga cleaning unit **37**B

and In electroplating unit **33** to fabricate a Cu/Ga/Cu/In stack. The anodes employed in the electroplating units may be inert anodes or they may be dissolvable anodes of Cu, In and Ga for Cu electrodeposition, In electrodeposition and Ga electrodeposition, respectively. The thicknesses of the Cu, In and Ga layers within the stack may range from 10 nm to 500 nm. Details of the cleaning or cleaning/drying units are not shown in FIG. **3**. However, established cleaning means, such as spraying the cleaning solution onto the part to be cleaned or immersing the part in the cleaning solution, may be used in these units. Air knives directing high speed air or inert gas onto the part to be dried may be used as the drying means. The drying gas may be pre-filtered and warmed for effective and fast drying.

[**0040**] We so far described an example of a system and process for roll-to-roll electrodeposition of stacks comprising Group IB and Group IIIA materials. Other processing units may be added to the electroplating system of FIG. **3** to extend its functionality as will be described next.

[**0041**] FIG. **4** depicts a roll-to-roll processing system **50** comprising a Group IB-IIIA electroplating unit **51** and a Group VIA material electroplating unit **62**. The Group IB-IIIA plating unit **51** electrodeposits the Group IB materials and Group IIIA materials on the flexible foil base **22** forming a metallic precursor film and may, for example, comprise all or most of the components of the electroplating system **30** of FIG. **3**. As an example, the Group IB-IIIA plating unit **51** may deposit Cu, Ga and In layers and may comprise the conditioning unit **34**, the cleaning unit **35**, the Cu electroplating unit **31**, the Cu cleaning unit **37**A, the Ga electroplating unit **32**, the Ga cleaning unit **37**B, and the In electroplating unit **33** of FIG. **3**. Instead of the cleaning/drying unit **38** of FIG. **3**, another cleaning unit (without drying) may be employed so that the flexible foil base **22** coated or electrochemically coated with Cu, Ga and In moves into the Group VIA material electroplating unit **62** with a clean and wet surface. In the Group VIA material electroplating unit **62**, a layer of at least one of Se, S and Te, preferably Se, is deposited onto the metallic precursor film. The flexible foil base with the "metallic precursor/Group VIA material" stack may then be passed through a final cleaning/drying module **63** and rolled onto the return spool **21**. Presence of a Group VIA material on the metallic precursor film comprising Cu, In and Ga has advantages. One such advantage is the protection provided by the Group VIA material to the surface of the metallic precursor film. Indium and Ga are soft, low melting materials and they are vulnerable to easy scratching during rolling and handling. By depositing a Group VIA material such as Se on the metallic precursor film this vulnerability is reduced or eliminated so that the flexible web may be rolled onto the return spool **21** safely. The thickness of the electroplated Group VIA material may be in the range of 10-2000 nm.

[**0042**] The roll-to-roll processing system of FIG. **4** may accommodate an optional annealing unit **64** as shown in FIG. **4**. When used, the annealing unit **64** will cause a reaction between the electrodeposited metallic precursor film and the electrodeposited Group VIA material and form a reacted precursor layer on the flexible foil base **22**. If the Group VIA material is Se, the reacted precursor layer may comprise phases such as Cu, In, Ga, Cu—Ga, Cu—In, In—Ga, Cu—Se, In—Se, Ga—Se, Cu—In—Se, Cu—Ga—Se, In—Ga—Se and Cu—In—Ga—Se, depending on the temperature applied in the annealing unit **64** and the time spent in the annealing unit **64**. The temperature applied by the annealing unit may be in the range of 100-550 C, preferably in the range of 200-450 C. After exiting the annealing unit **64**, the flexible web comprising the reacted precursor layer may be rolled onto the return spool **21** safely. A packing sheet may also be rolled along with it as described with reference to FIG. **2**. It should be noted that the Group VIA material electroplating unit **62** may be similar to the electroplating units described with reference to FIG. **3**. The annealing unit **64** may be similar to a design described in co-pending U.S. patent application Ser. No. 11/549,590 filed Oct. 13, 2006 entitled "Method and Apparatus For Converting Precursor Layers Into Photovoltaic Absorbers", entire contents of which are incorporated herein by reference.

[**0043**] The examples above employed a flexible foil base **22** such as the one depicted in FIG. **3**A. In the flexible foil base **22** of FIG. **3**A, the conductive layer **46** and the optional secondary layer **47** may be deposited on the flexible foil substrate **45** by various deposition techniques such as evaporation, sputtering etc. in a separate system. It is, however, possible to integrate another electroplating or electroless plating module to the systems of FIGS. **3** and **4** so that the flexible foil substrate **45** gets electroplated with at least one of a conductive layer or contact layer and a secondary layer before it moves into other process units such as the Group IB-IIIA electroplating unit of FIG. **4**. This way defects in the electroplated Cu, In and Ga layers that are due to defects in or on the contact layers (such as scratches, pinholes and other defects) are avoided since contact layers are freshly deposited and then get coated with Cu, Ga and In. The contact layer for this approach needs to comprise materials that can be electroplated or electroless plated and at the same time be a good ohmic contact to CIGS(S) material and not react extensively with S and/or Se. Such layers are disclosed in Applicant's co-pending U.S. application Ser. No. 11/266,013 filed Nov. 2, 2005 entitled "Technique and Apparatus for Depositing Layers of Semiconductors For Solar Cell and Modular Fabrication", and U.S. application Ser. No. 11/462,685 filed Aug. 4, 2004 entitled "Technique for Preparing Precursor Films and Compound Layers for Thin Film Solar Cell Fabrication and Apparatus Corresponding Thereto" and they comprise materials such as Ru, Ir and Os. It should be noted that by exposing the back side of the flexible foil substrate to a contact electroplating solution and deposition current, it is possible to electroplate a secondary layer on the back side of the substrate as the front face is plated by a contact layer.

[**0044**] In two-stage techniques, which involve deposition of a metallic precursor film comprising Cu, In and Ga and then reaction of the metallic precursor film with at least one of Se and S, individual thicknesses of the Cu, In and Ga layers need to be well controlled because they determine the final stoichiometry or composition of the compound layer after the reaction step. The roll-to-roll deposition approach of the present invention lends itself well for smart process control so that these thicknesses may be monitored and controlled using in-situ measurement devices such as X-ray fluorescence (XRF). XRF probes may be placed at various positions in the systems of FIG. **2**, FIG. **3** and FIG. **4** and these probes may monitor the deposited thicknesses of Cu, In, Ga and optionally Se layers. If there is any discrepancy between the target and deposited thickness of any of the Cu, In, Ga layers, the power supply controlling that thickness

may be sent a signal by the XRF tool to increase or decrease the plating current density to keep the film thickness within a targeted window. Such approaches are described in more detail in Applicant's co-pending U.S. Provisional Application Ser. No. 60/744,252 filed Apr. 4, 2006 entitled "Composition Control for Photovoltaic Thin Film Manufacturing".

[0045] Once the metallic precursor films, or the "metallic precursor/Group VIA material" stacks, or the reacted precursor layers of the present invention are formmed, reaction or further reaction of these layers with Group VIA materials may be achieved by various means. For example, these layers may be exposed to Group VIA vapors at elevated temperatures. These techniques are well known in the field and they involve heating the layers to a temperature range of 350-600° C. in the presence of at least one of Se vapors, S vapors, and Te vapors provided by sources such as solid Se, solid S, solid Te, H_2Se gas, H_2S gas etc. for periods ranging from 5 minutes to 1 hour. In another embodiment a layer or multi layers of Group VIA materials may be deposited on the metallic precursor layers and then heated up in a furnace or in a rapid thermal annealing furnace and like. Group VIA materials may be evaporated on, sputtered on or plated on the metallic precursor layers in a separate process unit. Alternately inks comprising Group VIA nano particles may be prepared and these inks may be deposited on the metallic precursor layers to form a Group VIA material layer comprising Group VIA nano particles. Dipping, spraying, doctor-blading or ink writing techniques may be employed to deposit such layers. Reaction may be carried out at elevated temperatures for times ranging from 1 minute to 30 minutes depending upon the temperature. As a result of reaction, the Group IBIIIAVIA compound is formed. It should be noted that reaction chambers may also be added to the apparatus of FIG. **4** or the annealing unit **64** may be a reaction unit to carry out the whole process in-line so that the flexible foil base with a fully formed CIGS(S) layer on its surface may be rolled onto the return spool **21**.

[0046] In the examples above, systems with horizontal web geometry have been discussed. It should be noted that the concepts of the present invention may be applied to systems where the flexible foil base travels in a vertical position or at any angle with respect to the horizontal plane. Depositions may be carried out on the horizontal web in either "deposit up" or "deposit down" manner. The flexible foil substrate may move from left to right or vice-versa. It may move continuously or in a stepwise manner. It may also move with an oscillating "back-and-forth" motion. It is possible to deposit some layers onto the flexible foil base as it is moved in one direction and then deposit more layer(s) as the foil is moved back in the reverse direction. DC, AC, pulsed or pulse-reverse type power supplies, among others, may be used for the electrodeposition steps.

[0047] Solar cells may be fabricated on the Group IBIIIAVIA compound layers of the present invention using materials and methods well known in the field. For example a thin (<0.1 microns) CdS layer may be deposited on the surface of the compound layer using the chemical dip method. A transparent window of ZnO may be deposited over the CdS layer using MOCVD or sputtering techniques. A metallic finger pattern is optionally deposited over the ZnO to complete the solar cell.

[0048] Although the present invention is described with respect to certain preferred embodiments, modifications thereto will be apparent to those skilled in the art.

What is claimed is:

1. A system for forming an absorber structure for solar cells on a front surface of a continuous flexible workpiece as the continuous flexible workpiece is advanced through units of the system, comprising:

a conditioning unit to condition the front surface of the continuous flexible workpiece to form activated surface portions, wherein the activated surface portions present a consistently active surface substantially along the continuous flexible workpiece for electroplating;

a first electroplating unit to form a first layer of a precursor stack by electroplating a metal belonging to one of Group IB and Group IIIA over one of the activated surface portions of the continuous flexible workpiece as the continuous flexible workpiece is advanced through the first electroplating station;

a first cleaning unit to clean the first layer deposited in the first electroplating unit;

a second electroplating unit to form a second layer of the precursor stack by electroplating another metal belonging to the other of the Group IB and Group IIIA over the first layer as the continuous flexible workpiece is advanced through the second electroplating units and while the first layer is continued to be electroplated onto a following one of the activated surface portions of the surface of the continuous flexible workpiece in the first electroplating unit, wherein the first layer is different from the second layer;

a second cleaning unit to clean the second layer deposited in the second electroplating unit; and

a moving assembly to hold and linearly move the continuous flexible workpiece through the units of the system, wherein the moving assembly comprises a feed spool to unwrap and feed unprocessed portions of the continuous flexible workpiece into the system and a take-up spool to receive processed portions and wrap them around.

2. The system of claim 1 further comprising a third electroplating unit to form a third layer by electroplating a further metal belonging to one of the Group IB and Group IIIA over the second layer to obtain the precursor stack as the continuous flexible foil is advanced through the first, second and third electroplating stations and while the second layer is continued to be electroplated in the second electroplating station on the first layer that is electroplated on the following activated portion of the surface of the continuous flexible workpiece, and while the first layer is continued to be electroplated onto a further following one of the activated surface portions of the surface of the continuous flexible workpiece in the first electroplating station, wherein the third layer is different from the first and second layers.

3. The system of claim 2 further comprising one of a cleaning-drying unit to clean and dry the third layer and a third cleaning unit to clean the third layer deposited in the third electrodeposition unit.

4. The system of claim 3 further comprising an annealing unit to react the first, second and third layers.

5. The system of claim 3 further comprising a fourth electrodeposition unit to deposit a fourth layer of a Group VIA material over the third layer.

6. The system of claim 5, wherein the Group VI material includes one of Se, S and Te.

7. The system of claim 5 further comprising a cleaning-drying unit to clean and dry the fourth layer and an annealing unit to react the first, second, third and fourth layers.

8. The system of claim 1, wherein the conditioning unit comprises at least one of:

an electrotreating chamber having an electrotreating solution and electrode that can be anodically or cathodically polarized with respect to the front surface of the continuous flexible workpiece to form the activated portions,

a deposition chamber to deposit a seed layer over the front surface of the continuous flexible workpiece a pickling chamber to treat the front surface of the continuous flexible workpiece to form the activated portions, and

an etching chamber to etch the front surface of the continuous flexible workpiece to form the activated portions.

9. The system of claim 1, wherein the Group IB material includes Cu and wherein the first Group IIIA material includes one of Ga and In.

10. The system of claim 1 further comprising a packing supply spool to provide a continuous packing sheet to place onto the processed portions as the continuous flexible workpiece is wrapped around the take-up spool.

11. The system of claim 9 further comprising a deposition monitoring unit to monitor and control the thickness of deposited first, second and third layers.

12. The system of claim 11 wherein the deposition monitoring unit provides a feedback signals to each of the first, second and third electrodeposition units to cause the thicknesses of deposited first, second and third layers to converge toward a predetermined thickness for each of the first, second and third layers.

13. The system of claim 12 wherein the convergence is to maintain target ratios of Cu/In+Ga and Ga/In+Ga.

14. A process of forming a precursor stack on a frontside of a continuous flexible workpiece using a system including a moving assembly, wherein the frontside includes a conductive layer, comprising:

moving the continuous flexible workpiece into and sequentially through a conditioning unit, an activated surface cleaning unit, a first electroplating unit, a first cleaning unit, a second electroplating unit, a second cleaning unit, a third electroplating unit, and a cleaning-drying unit by feeding previously unrolled portions of the continuous flexible workpiece from an input end of the system;

conditioning the surface of the conductive layer in the conditioning unit to form an activated surface portion, wherein the activated surface portion presents a consistently uniform surface along substantially an entirety of the continuous flexible workpiece for electroplating;

cleaning the activated surface portion in the activated surface cleaning unit;

forming a precursor stack over the activated surface portion after cleaning the activated surface portion, comprising:

forming a first material layer over the activated surface portion by electrodepositing one of a Group IB material and a Group IIIA material in the first electroplating unit;

cleaning the first material layer in the first cleaning unit;

forming a second material layer over the first material layer by electrodepositing the other of the Group IB material and the Group IIIA material in the second electroplating unit, wherein the second material layer is different from the first material layer;

cleaning the second material layer in the second cleaning unit;

forming a third material layer over the second material layer by depositing another of the Group IB material and the Group IIIA material in the third electroplating unit, wherein the third material layer is different from the first and the second material layers; and

cleaning and drying the precursor stack in the cleaning-drying unit; and

taking up and wrapping processed portion of the continuous flexible workpiece at an output end of the system.

15. The process of claim 14 further comprising:

cleaning the precursor stack in a third cleaning unit prior to cleaning and drying; and

forming a fourth material layer over the precursor stack by depositing at least one Group VIA material from a fourth deposition unit; and wherein the moving the continuous flexible workpiece into and sequentially through includes the third cleaning unit and the fourth deposition unit.

16. The process of claim 15 further comprising reacting the precursor stack and the fourth layer in an annealing unit; and wherein the moving the continuous flexible workpiece into and sequentially through includes the annealing unit.

17. The process of claim 16, wherein the at least one Group VI material comprises one of Se, S and Te.

18. The process of claim 15, wherein the at least one Group VI material comprises one of Se, S and Te.

19. The process of claim 15, wherein the at least one Group VIA material is deposited by one of dipping the precursor stack into an ink solution including nano-particles of the at least one Group VIA material and depositing by electrodeposition the at least one Group VIA material onto the precursor stack.

20. The process of claim 14 further comprising reacting the precursor stack in an annealing unit with at least one Group VIA material after cleaning and drying; and wherein the moving the continuous flexible workpiece into and sequentially through includes the annealing unit.

21. The process of claim 14 wherein conditioning comprises one of electrotreating the conductive layer in a process solution with respect to an electrode by applying one of cathodic and anodic polarization deposit a seed layer onto the front surface of the continuous flexible workpiece and

pickling the front surface of the continuous flexible workpiece to form the activated portion.

22. The process claim 14 wherein the conditioning comprises depositing a seed layer on the contact layer.

23. The process of claim 14, wherein the Group IB material includes Cu and wherein the Group IIIA material includes one of Ga and In.

24. The process of claim 14 further comprising, forming a fifth material layer after forming the second layer, wherein the fifth layer and the first layer are the same, and forming a sixth layer after forming the third layer, wherein the sixth and the second layer are the same.

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