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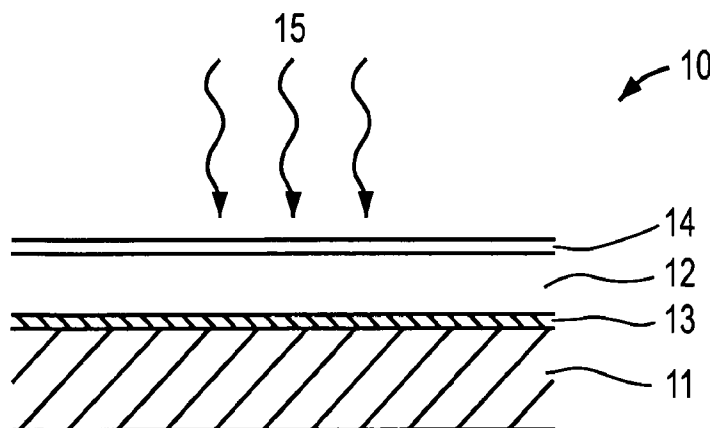
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(57) Abstract: A roll to roll system for forming an absorber structure for solar cells on a flexible foil as the flexible foil is advanced through units of the system and by unwrapping from a supply spool and wrapping around a take-up spool. Surface 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.

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ROLL-TO-ROLL ELECTROPLATING FOR PHOTOVOLTAIC FILM MANUFACTURING

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority to Provisional Application Serial No. 60/862,164 filed on October 19, 2006.

FIELD OF THE INVENTION

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

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.

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 $\text{CuIn}_{1-x}\text{Ga}_x(\text{S}_y\text{Se}_{1-y})_k$, where $0 \leq x \leq 1$, $0 \leq y \leq 1$ 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.

The structure of a conventional Group IBIIIA VIA compound photovoltaic cell such as a $\text{Cu}(\text{In,Ga,Al})(\text{S,Se,Te})_2$ thin film solar cell is shown in Figure 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 $\text{Cu}(\text{In,Ga,Al})(\text{S,Se,Te})_2$, 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 Figure 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 Figure 1 may also be inverted if substrate is transparent. In that case light enters the device from the substrate side of the solar cell.

In a thin film solar cell employing a Group IBIIIA VIA 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 $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ absorber layer, for example, the efficiency of the device is a function of the molar ratio of $\text{Cu}/(\text{In}+\text{Ga})$. 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 $\text{Ga}/(\text{Ga}+\text{In})$ molar ratio. In general, for good device performance $\text{Cu}/(\text{In}+\text{Ga})$ molar ratio is kept at around or below 1.0. As the $\text{Ga}/(\text{Ga}+\text{In})$ 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 $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$, a more accurate formula for the compound is $\text{Cu}(\text{In,Ga})(\text{S,Se})_k$, 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.

The first technique used to grow Cu(In,Ga)Se₂ 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.

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 CuInSe₂ 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.

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 CuInSe₂ 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. 4,798,660. More recently U.S. Patent 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. Patent 6,092,669 described sputtering-based equipment and method for producing such absorber layers.

One prior art method described in U.S. Patent 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).

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

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.

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.

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.

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.

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

FIG. 1 is a cross-sectional view of a solar cell employing a Group IBIIIIVIA absorber layer.

FIG. 2 shows a roll to roll electrodeposition system of the present invention.

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

FIG. 3A shows a structure of the flexible foil base.

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

FIG. 5 shows a flow chart of an embodiment of a process using roll to roll system

DETAILED DESCRIPTION

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

Figure 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 24A, 24B. 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.

Flow chart 100 shown in Figure 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.

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 2ft/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.

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%.

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 110.

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.

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.

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.

Figure 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 Figure 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 Figure 3 with the electroplating system 30 comprising one of each of a Cu electroplating unit, a Ga electroplating unit and an In electroplating unit.

In the electroplating system 30 of Figure 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 Figure 3A. 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 45A 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 μm 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 46A of the conductive layer 46 comprises at least one of Ru, Ir and Os for better nucleation of the electroplated layers.

In this example, electrodeposition is carried out on the free surface 46A of the conductive layer 46. The back surface 45B 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 46A 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 selenized 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.

Referring back to Figure 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 46A of the conductive layer 46 in Figure 3A) is conditioned to render it ready for electrodeposition with Cu. Such conditioning may involve exposing the free surface 46A to an acidic or basic solution for etching and/or activation, applying a cathodic or anodic voltage to the free surface 46A with

respect to an electrode while both the electrode and the free surface 46A are exposed to an electrolyte, electrodepositing a seed layer on the free surface 46A, or simply rinsing and wetting the free surface 46A 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 46A 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 Serial No. 11/266,013 filed November 2, 2005 entitled "Technique and Apparatus for Depositing Layers of Semiconductors For Solar Cell and Modular Fabrication", and U.S. Application Serial No. 11/462,685 filed August 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.

Once a section of the free surface 46A 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 46A (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 36A which may be circulated between a first reservoir 36AA and a first chemical cabinet 36A'. The Cu plating bath 36A may be filtered and replenished during circulation or while in the first chemical cabinet 36A'. 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 36A' 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 40A is placed in the Cu plating bath 36A and a potential difference is

applied between the first anode 40A and the portion of the conductive layer 46 within the Cu electroplating unit 31, to deposit Cu on the portion of the free surface 46A that is exposed to the Cu plating bath 36A as the flexible foil base 22 is moved.

The portion of the flexible foil base 22 processed in the Cu electroplating unit 31, passes through the Cu cleaning unit 37A 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 36B which may be circulated between a second reservoir 36BB and a second chemical cabinet 36B'. The Ga plating bath 36B may be filtered and replenished during circulation or while in the second chemical cabinet 36B'. 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 36B' 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 40B is placed in the Ga plating bath 36B and a potential difference is applied between the second anode 40B 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 36B as the flexible foil base 22 is moved.

The portion of the flexible foil base processed in the Ga electroplating unit 32, passes through the Ga cleaning unit 37B 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 36C which may be circulated between a third reservoir 36CC and a third chemical cabinet 36C'. The In plating bath 36C may be filtered and replenished during circulation or while in the third chemical cabinet 36C'. 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 36C' 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 40C is placed in the In plating bath 36C and a potential difference is applied between the third anode 40C 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 36C 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.

It should be noted that additional process units may be added to the electroplating system 30 of Figure 3. For example, another Cu electroplating unit and another cleaning unit may be inserted between the Ga cleaning unit 37B 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 10nm to 500 nm. Details of the cleaning or cleaning/drying units are not shown in Figure 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.

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 Figure 3 to extend its functionality as will be described next.

Figure 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 Figure 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 37A, the Ga electroplating

unit 32, the Ga cleaning unit 37B, and the In electroplating unit 33 of Figure 3. Instead of the cleaning/drying unit 38 of Figure 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.

The roll-to-roll processing system of Figure 4 may accommodate an optional annealing unit 64 as shown in Figure 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 Figure 2. It should be noted that the Group VIA material electroplating unit 62 may be similar to the electroplating units described with reference to Figure 3. The annealing unit 64 may be similar to a design described in co-pending U.S. Patent Application Serial No. 11/549,590 filed October 13, 2006 entitled “Method and Apparatus For Converting Precursor Layers Into Photovoltaic Absorbers”, entire contents of which are incorporated herein by reference.

The examples above employed a flexible foil base 22 such as the one depicted in Figure 3A. In the flexible foil base 22 of Figure 3A, 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 Figure 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-III A electroplating unit of Figure 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 Serial No. 11/266,013 filed November 2, 2005 entitled "Technique and Apparatus for Depositing Layers of Semiconductors For Solar Cell and Modular Fabrication", and U.S. Application Serial No. 11/462,685 filed August 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.

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 Figure 2, Figure 3 and Figure 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 Serial No. 60/744,252 filed April 4, 2006 entitled "Composition Control for Photovoltaic Thin Film Manufacturing".

Once the metallic precursor films, or the "metallic precursor/Group VIA material" stacks, or the reacted precursor layers of the present invention are formed, 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, H₂Se gas, H₂S 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 Figure 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.

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.

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.

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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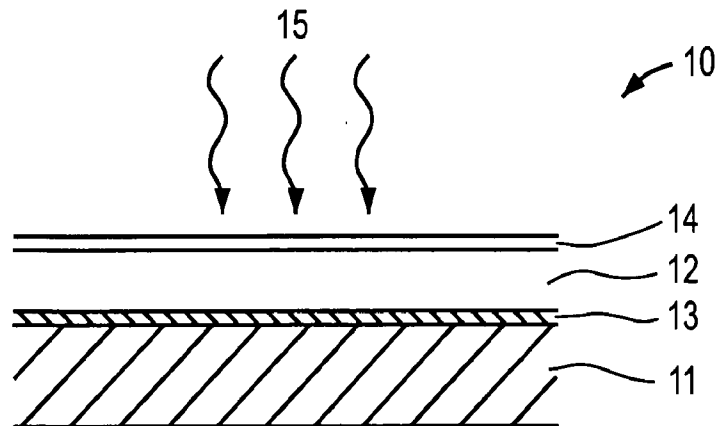


FIG. 1

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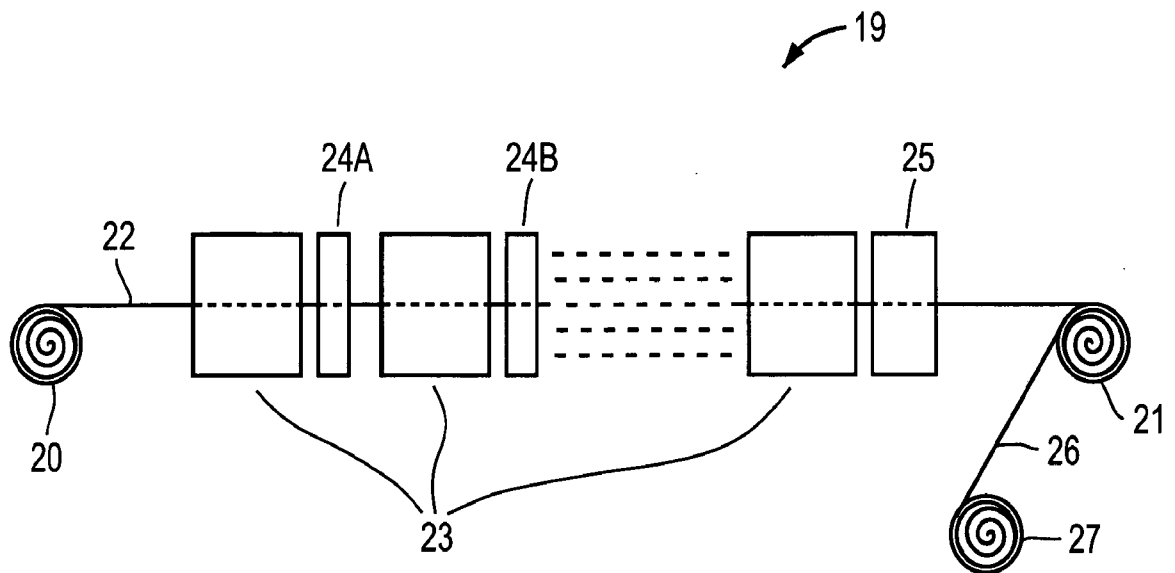


FIG. 2

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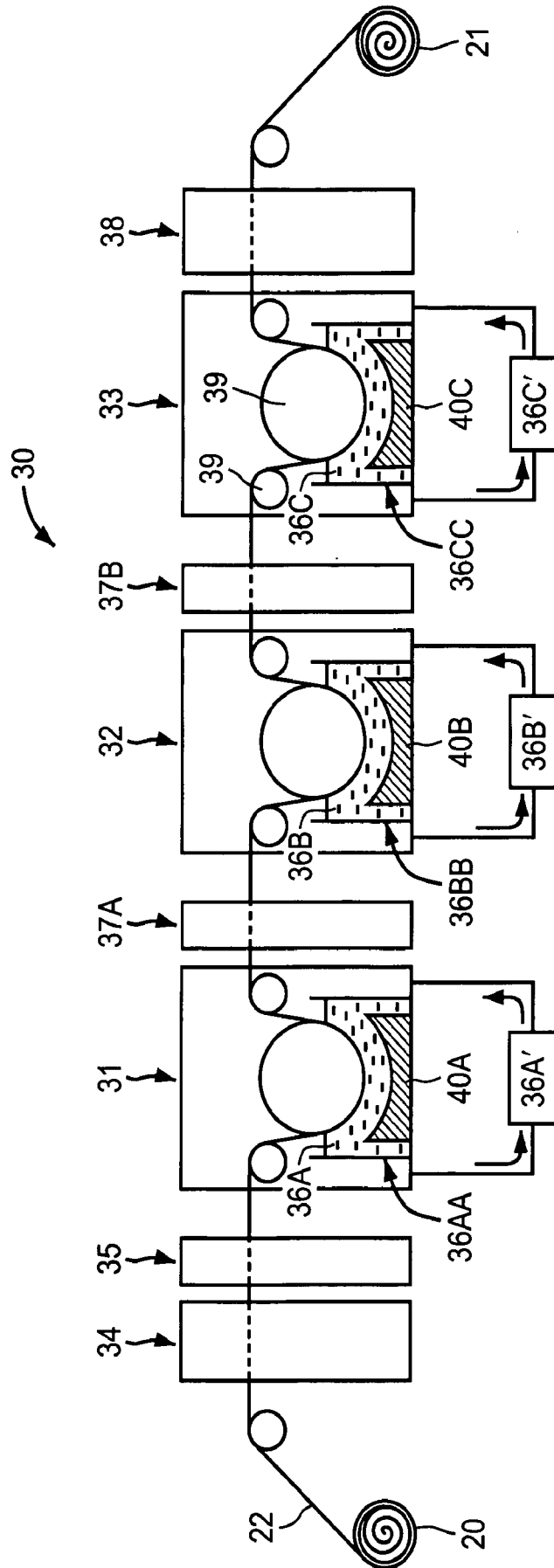


FIG. 3

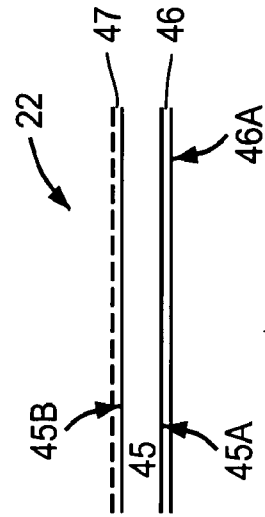


FIG. 3A

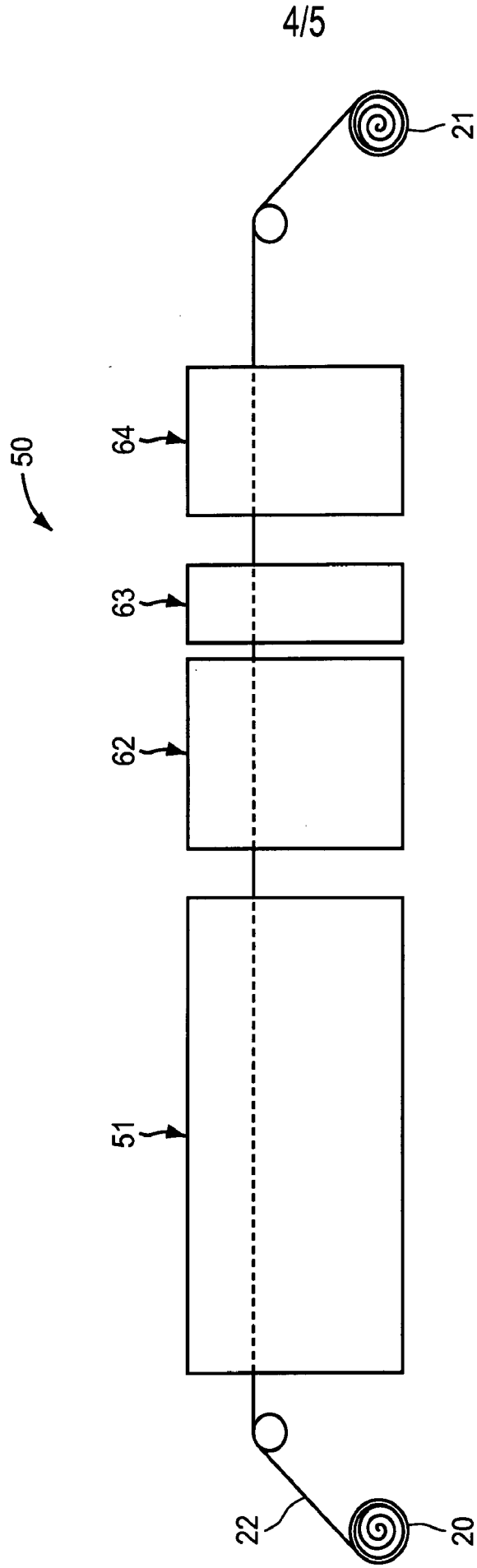


FIG. 4

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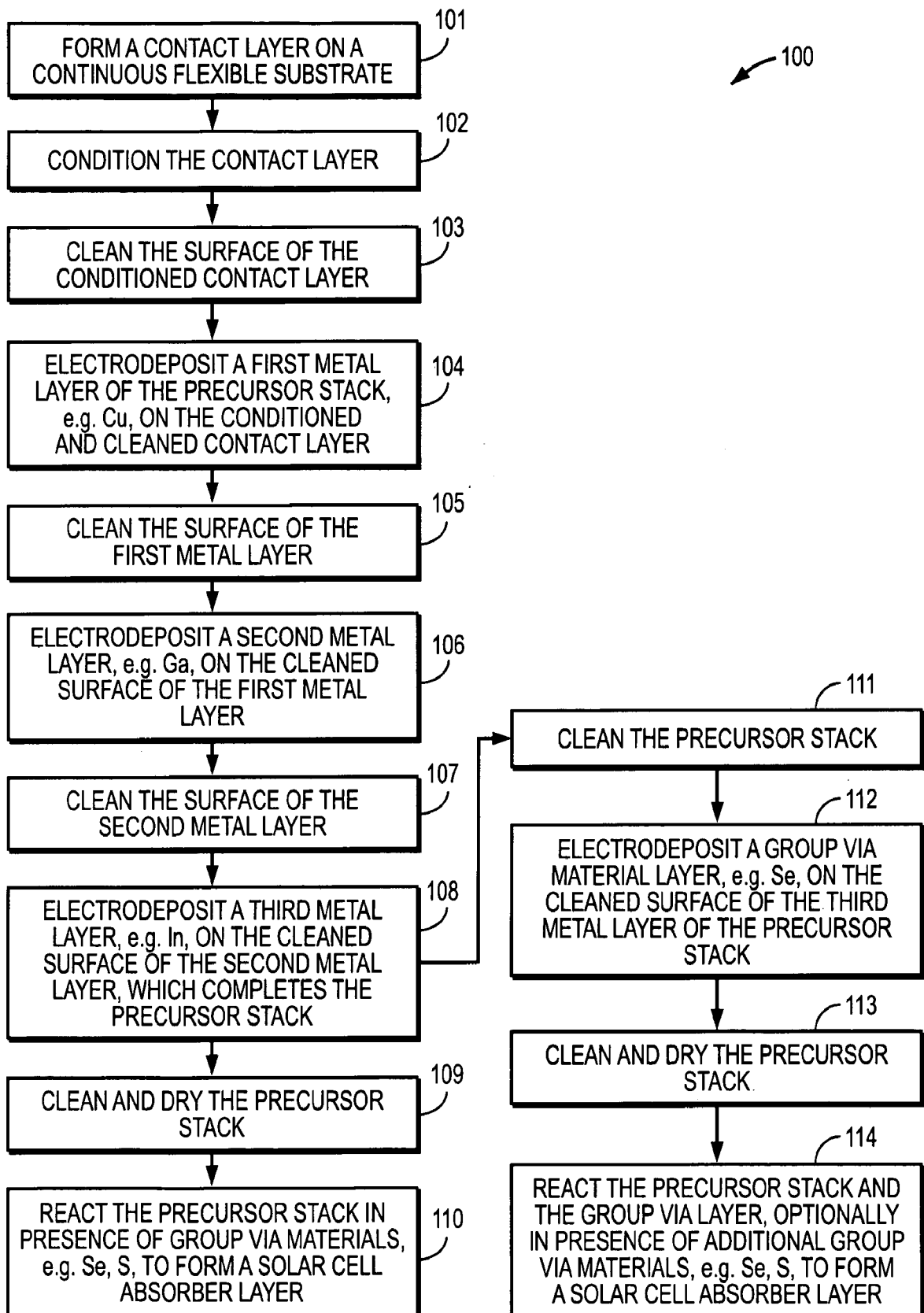


FIG. 5