



US 20080023336A1

(19) **United States**

(12) **Patent Application Publication**

(10) **Pub. No.: US 2008/0023336 A1**

Basol

(43) **Pub. Date:**

Jan. 31, 2008

(54) **TECHNIQUE FOR DOPING COMPOUND LAYERS USED IN SOLAR CELL FABRICATION**

Publication Classification

(51) **Int. Cl.**
C25D 5/10 (2006.01)

(76) Inventor: **Bulent M. Basol**, Manhattan Beach, CA (US)

(52) **U.S. Cl.** **205/182; 205/170**

Correspondence Address:
PILLSBURY WINTHROP SHAW PITTMAN LLP
P.O. BOX 10500
MCLEAN, VA 22102 (US)

(57) **ABSTRACT**

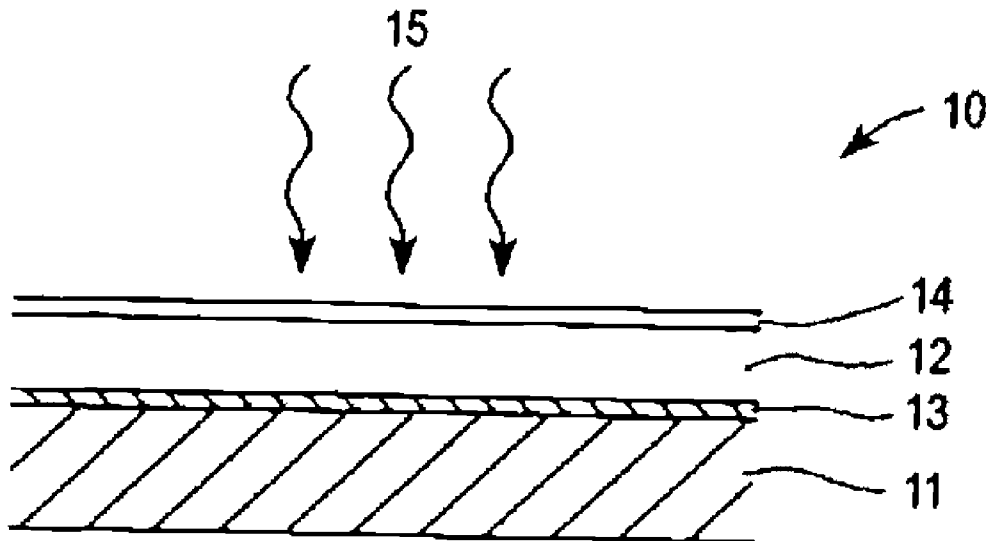
The present invention includes methods and apparatus therefrom for preparing thin films of doped semiconductors for radiation detector and photovoltaic applications, and particularly method and apparatus that increase dopants of alkali metals in Group IBIIIAVIA layers. In a particular aspect, the present invention includes a method of preparing a doped Group IBIIIAVIA absorber layer for a solar cell, with the absorber layer being formed by reaction, with a Group VIA material, of a metallic stack with a plurality of layers, in which each layer contains a concentration of an alkali metal selected from the group of Na, K and Li.

(21) Appl. No.: **11/829,052**

(22) Filed: **Jul. 26, 2007**

Related U.S. Application Data

(60) Provisional application No. 60/820,479, filed on Jul. 26, 2006.



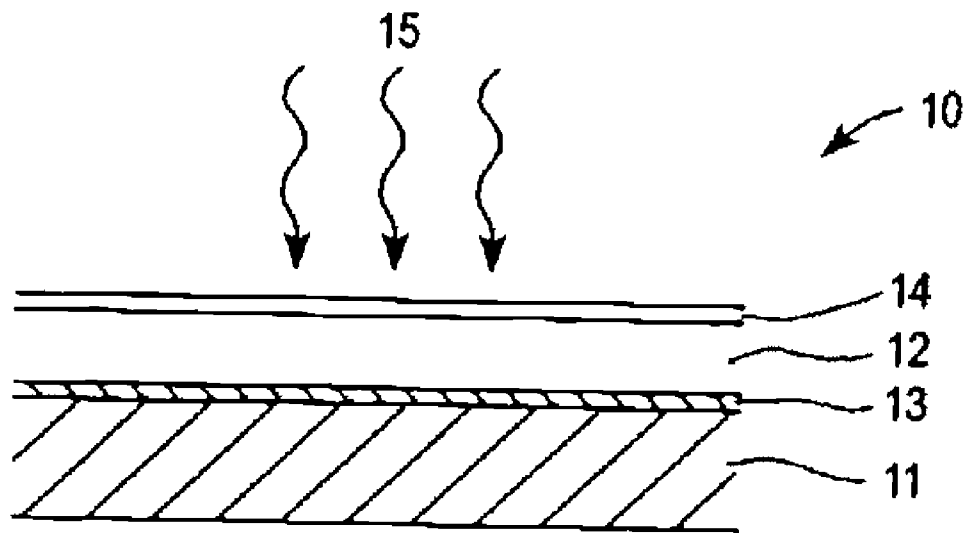


FIG. 1

TECHNIQUE FOR DOPING COMPOUND LAYERS USED IN SOLAR CELL FABRICATION

CLAIM OF PRIORITY

[0001] This application claims priority to and incorporates herein by reference U.S. Provisional Appln. Ser. No. 60/820,479 filed Jul. 26, 2006 entitled "Technique for Doping Compound Layers Used in Solar Cell Fabrication"; and is related to U.S. application Ser. No. 11/081,308 filed Mar. 15, 2005 entitled "Technique and Apparatus for Depositing Thin Layers of Semiconductors for Solar Cell Fabrication"; 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 Module Fabrication"; U.S. application Ser. No. 11/462,685 filed Aug. 4, 2006 entitled "Technique for Preparing Precursor Films and Compound Layers For Thin Film Solar Cell Fabrication"; and U.S. application Ser. No. 11/535,927 filed Sep. 27, 2006 entitled "Efficient Gallium Thin Film Electroplating Methods and Chemistries".

FIELD OF THE INVENTION

[0002] The present invention relates to method and apparatus for preparing thin films of doped semiconductors 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 IBIII AVIA compound semiconductors comprising some of the Group IB (Cu, Ag, Au), Group IIIA (B, Al, Ga, In, Ti) 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 $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ 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%. Among the family of compounds, best efficiencies have been obtained for those containing both Ga and In, with a Ga amount in the 15-25%. 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 IBIII AVIA compound photovoltaic cell such as a $\text{Cu}(\text{In,Ga,Al})(\text{S,Se,Te})_2$ 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, 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 or a contact layer, which is previously deposited on the substrate 11 and which acts as the electrical ohmic contact to the device. The most commonly used contact layer or conductive layer in the solar cell structure of FIG. 1 is Molybdenum (Mo). If the substrate itself is a properly selected conductive material such as a Mo foil, 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. The conductive layer 13 may also act as a diffusion barrier in case the metallic foil is reactive. For example, metallic foils comprising materials such as Al, Ni, Cu may be used as substrates provided a barrier such as a Mo layer is deposited on them protecting them from Se or S vapors. The barrier is often deposited on both sides of the foil to protect it well. 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. The preferred electrical type of the absorber film 12 is p-type, and the preferred electrical type of the transparent layer 14 is n-type. However, an n-type absorber and a p-type window layer can also be utilized. The preferred device structure of FIG. 1 is called a "substrate-type" structure. A "superstrate-type" structure can also be constructed by depositing a transparent conductive layer on a transparent superstrate such as glass or transparent polymeric foil, and then depositing the $\text{Cu}(\text{In,Ga,Al})(\text{S,Se,Te})_2$ absorber film, and finally forming an ohmic contact to the device by a conductive layer. In this superstrate structure light enters the device from the transparent superstrate side. A variety of materials, deposited by a variety of methods, can be used to provide the various layers of the device shown in FIG. 1. It should be noted that although the chemical formula of copper indium gallium sulfo-selenide 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, $\text{Cu}(\text{In,Ga})$ means all compositions from CuIn to CuGa . Similarly, $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ 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.

[0006] The first technique that yielded high-quality $\text{Cu}(\text{In,Ga})\text{Se}_2$ films for solar cell fabrication was co-evaporation of Cu, In, Ga and Se onto a heated substrate in a vacuum chamber. This is an approach with low materials utilization and high cost of equipment.

[0007] Another technique for growing $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ type compound thin films for solar cell applications is a two-stage process where metallic components of the $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ 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 layers of Cu and In are first deposited on a substrate and then this stacked precursor layer is reacted with Se at elevated temperature. If the reaction atmosphere also contains sulfur, then a $\text{CuIn}(\text{S,Se})_2$ 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 $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ absorber.

[0008] Sputtering and evaporation techniques have been used in prior art approaches to deposit the layers containing the Group IB and Group IIIA components of the precursor stacks. In the case of CuInSe_2 growth, for example, Cu and In layers were sequentially sputter-deposited on a substrate and then the stacked film was heated in the presence of gas containing Se at elevated temperature for times typically longer than about 30 minutes, 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 layer(s) and an In layer to form a Cu—Ga/In stack on a metallic back electrode layer and then reacting this precursor stack film with one of Se and S to form the absorber layer. U.S. Pat. No. 6,092,669 described sputtering-based equipment for producing such absorber layers.

[0009] One prior art method described in U.S. Pat. No. 4,581,108 utilizes a low cost electrodeposition approach for metallic precursor preparation. In this method a Cu layer is first electrodeposited on a substrate covered with Mo. This is then followed by electrodeposition of an In layer and heating of the deposited Cu/In stack in a reactive atmosphere containing Se to obtain CIS. Prior investigations on possible dopants for Group IBIII AVIA compound layers have shown that alkali metals, such as Na, K, and Li, affect the structural and electrical properties of such layers. Especially, inclusion of Na in CIGS layers was shown to be beneficial for increasing the conversion efficiencies of solar cells fabricated on such layers. Inclusion of Na into CIGS layers was achieved by various ways. For example, Na diffuses into the CIGS layer from the substrate if the film is grown on a Mo contact layer deposited on a Na-containing soda-lime glass substrate. This is, however, an uncontrolled process and causes non-uniformities in the CIGS layers depending on how much Na diffuses from the substrate through the Mo contact layer. Therefore the amount of Na doping is a strong function of the nature of the Mo layer such as its grain size, crystalline structure, chemical composition, thickness, etc. In another approach (see for example, U.S. Pat. No. 5,626,688), a diffusion barrier is deposited on the soda-lime glass substrate to stop possible Na diffusion from the substrate into the absorber layer. A Mo contact film is then deposited on the diffusion barrier. An interfacial layer comprising Na is formed on the Mo surface. The CIGS film is then grown over the Na containing interfacial layer. During the growth period, Na from the interfacial layer diffuses into the CIGS layer and dopes it. The most commonly used interfacial layer material is NaF, which is evaporated on the Mo surface before the deposition of the CIGS layer (see, for example, Granath et al., *Solar Energy Materials and Solar Cells*, vol: 60, p: 279 (2000)).

[0010] It should be noted that the method described above is commonly used for doping CIGS layers grown by physical vapor deposition (PVD) techniques. It is straight forward to deposit a Na-containing interfacial layer, such as a NaF interfacial layer, on a substrate by a PVD technique such as evaporation or sputtering and then grow a CIGS film over the interfacial layer by another PVD step such as co-evaporation, sputtering etc. Alternately, it is also possible to deposit, by a PVD technique, a precursor layer comprising Cu, In and Ga onto the Na-containing interfacial layer and

then react the precursor layer with Se and/or S to form a Na-doped $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ layer. In wet coating approaches such as electroless plating and electroplating this may not be possible. Since such wet techniques are surface sensitive and may be carried out of aqueous solutions nucleation on materials such as NaF and NaCl may not be good or even possible. Electrodeposition, for example, requires a conductive substrate surface. Therefore, a precursor layer such as a Cu/In/Ga stack or a precursor layer comprising Cu, In, Ga and optionally Se may not be electrodeposited in a reliable and repeatable manner on substrates comprising a Na source on their surface. Furthermore, PVD techniques typically used to deposit Na-containing interfacial layers are expensive methods that increase cost of production. Control of the thickness of the Na-containing interfacial layer is critical since studies showed that excessive amount of Na such as more than 2 atomic percent may deteriorate properties of Group IBIII AVIA compound layers such as their crystalline properties and mechanical properties, especially their adhesion to their substrate.

[0011] As the review above demonstrates, controlled doping of Group IBIII AVIA compound layers with alkali metals improve their quality in terms of yielding higher efficiency solar cell devices, however, low cost approaches are needed to include such dopants into the growing film in a controlled manner. There is especially a need to develop techniques of introducing alkali metals in Group IBIII AVIA layers grown on a base utilizing a processing technique comprising at least one wet deposition step.

SUMMARY OF THE INVENTION

[0012] The present invention relates to method and apparatus for preparing thin films of doped semiconductors for radiation detector and photovoltaic applications, and particularly method and apparatus that increase dopants of alkali metals in Group IBIII AVIA layers.

[0013] In one aspect, the present invention includes methods and apparatus therefrom for preparing thin films of doped semiconductors for radiation detector and photovoltaic applications, and particularly method and apparatus that increase dopants of alkali metals in Group IBIII AVIA layers.

[0014] In a particular aspect, the present invention includes a method of preparing a doped Group IBIII AVIA absorber layer for a solar cell, with the absorber layer being formed by reaction, with a Group VIA material, of a metallic stack with a plurality of layers, in which each layer contains a concentration of an alkali metal selected from the group of Na, K and Li.

[0015] In another aspect, the present invention includes a method of electrodepositing a stack comprising Cu, In, Ga and Se and reaction of this stack to form a doped Group IBIII AVIA absorber layer for a solar cell, the stack being electrodeposited out of solutions comprising an alkali metal selected from the group of Na, K and Li.

[0016] In a preferred embodiment, the alkali metal is Na.

BRIEF DESCRIPTION OF THE DRAWINGS

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

DETAILED DESCRIPTION

[0018] There are various ways of growing Group IBIII AVIA compound films such as $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ compound

layers utilizing wet techniques such as electrodeposition. In one approach all the group IB and Group IIIA elements of the compound, i.e. Cu, In and Ga are electroplated on a base in the form of discrete layers forming a stacked precursor layer with a structure such as Cu/Ga/In, or Cu/In/Ga, or Cu/Ga/Cu/In, or Cu/In/Cu/Ga, etc. This precursor layer is then reacted with at least one of S and Se to form the Cu(In,Ga)(Se,S)₂ compound layer. It is also possible to use a hybrid approach where only some of the constituents of the compound are electrodeposited. For example, one can deposit Cu by PVD and Ga and In by electrodeposition to form a precursor layer comprising Cu, In and Ga and then react this precursor layer with at least one of Se and S to form the compound. The present invention achieves controlled doping of the compound layer by including at least one alkali metal in the formulation of the plating bath of the electrodeposited constituent. Since the plating potentials of Na, K and Li are much higher than plating potentials of Cu, In, and Ga; alkali metals do not directly plate on the base along with the depositing species such as Cu, In, and Ga. Instead they can be trapped or included in the deposits, typically in amounts of less than 1 atomic percent. This is a self limiting process and avoids buildup of excessive concentrations of alkali metals in the precursor and therefore avoids the Na-containing interfacial layer thickness control problem associated with prior-art techniques. The concentration of alkali metals in the electrodeposited films may be fine tuned by controlling the amount of alkali metals added to the plating electrolyte.

[0019] It should be noted that alkali metals may be added into all the plating baths used for deposition of Cu, In and Ga sub-layers, or they may be added to only one or some of them. This offers another knob to control the alkali metal concentration in atomic level. For example, if a Cu/Ga/In or Cu/In/Ga stack is electroplated from three different baths, one for Cu, one for In and one for Ga deposition, all three baths may contain alkali metals such as Na, or only one or two of the baths may contain this dopant. This way Na atomic concentration in the final absorber film (after the stack precursor is reacted with a Group VIA material) may be controlled in the range of 10^{16} - 10^{21} atoms/cc range. Alkali metals may be added into the bath using alkali-containing chemicals such as NaOH, NaCl, NaF, Na-citrate, Na-sulfate, Na-nitrate, Na-acetate, KOH, KCL, KF, K-citrate, K-acetate, K-sulfate, K-nitrate, etc. The concentration of alkali species in the bath may change from about 50 ppm to about 3 molar, preferably in the range of 500 ppm and 2 molar.

[0020] In a first embodiment of the present invention a metallic stack comprising Cu, In and Ga is formed by electroplating each element separately in the form of discrete layers on a base such as a glass/Mo, glass/Mo/Ru, foil/Mo or foil/Mo/Ru structure. Doping with an alkali element is achieved by including the alkali element in the electroplating bath of at least one of Cu, In and Ga. The stack may have a structure such as Cu/Ga/In, Cu/Ga/Cu/In, Ga/Cu/In, In/Cu/Ga, Cu/In/Ga, In/Cu/Ga/Cu, In/Cu/Ga/In, In/Cu/In/Ga, In/Cu/Ga/In/Cu, In/Cu/In/Ga/Cu, Ga/Cu/In/Cu, Ga/Cu/In/Ga, Ga/Cu/Ga/In, Ga/Cu/In/Ga/Cu, Ga/Cu/Ga/In/Cu, Ga/In/Cu, Ga/In/Cu/Ga, Ga/In/Cu/In, Ga/In/Cu/Ga/Cu, Ga/In/Cu/In/Cu, Ga/In/Ga/Cu, In/Ga/Cu, In/Ga/Cu/In, In/Ga/Cu/Ga/Cu, and In/Ga/Cu/In/Cu. etc. An alkali such as Na may be added into at least one of the Cu electrolyte, the Ga electrolyte and the In electrolyte. Copper electrolyte

or solution may comprise a Cu salt such as Cu-chloride, Cu-sulfate and Cu-citrate. Gallium electrolyte or solution may comprise a Ga salt such as Ga-chloride, Ga-sulfate and Ga-citrate. Indium electrolyte or solution may comprise an In salt such as In-chloride, In-sulfate, In-sulfamate and In-citrate. Sodium may be added to any one of these electrolytes in the form of NaOH, NaCl, Na-citrate, Na-sulfate, NaF, Na-nitrate, etc. At high Na concentrations such as 2-3M, the viscosity of the solution increases. Therefore, mass transport slows down. The amount of Na salt may be optimized based on its doping effect as well as the other factors such as viscosity. A practical range for the Na salt may be 500 ppm-2M. Although an increase in the Na content of the electroplated stack was seen by including Na in at least one of the Cu electrolyte, In electrolyte and Ga electrolyte, it was observed that best results, in terms of doping the resultant CIGS layer, were obtained if Na was included in all of the Cu, In and Ga containing plating electrolytes. This way Na content of over 0.01% could be obtained. For example, when a Cu/Ga/Cu/In stack was electroplated out of Na-free Cu, Ga and In electrolytes and then selenized to form a CIGS absorber layer, solar cells made on such absorber layer had efficiency values of 3-4%. By adding Na in one or two of the Cu electrolyte, In electrolyte and Ga electrolyte, resulting efficiency of the solar cells increased to the 4-6% range. When Na was included in all of the electrolytes, cells of about 8% efficiency could be fabricated. Sodium content in the electrodeposited stacks was also confirmed through Secondary Ion Mass Spectroscopy (SIMS) technique. Films or stacks electroplated out of Na-free electrolytes yielded Na concentrations in the order of 10^{15} atoms/cc. Adding Na into the electrolyte of the Cu deposition bath gave Na levels in the order of 10^{17} atoms/cc in the electroplated film. Adding Na into the plating electrolytes of Cu, In and Ga, on the other hand, raised the Na level in the plated stack to around 10^{19} - 10^{20} atoms/cc as measured by SIMS analysis. It should be appreciated that for efficient doping of the reacted film, it is preferable for the metallic stack or precursor to contain more than about 10^{19} atoms/cc of alkali metal.

[0021] In the examples above, each layer or sub-layer within the metallic stack is made of a pure element, i.e. Cu, In or Ga. It should be noted that, it is within the scope of the invention to include alloys and/or mixtures in the metallic stack. For example, at least one of the Cu sub-layers in the above examples may be replaced with a Cu—Ga alloy or mixture sub-layer, or a Cu—In alloy or mixture sub-layer. Similarly, any Ga or In layer may be replaced with an In—Ga mixture or alloy sub-layer. In these cases the alkali dopant is added into the plating electrolyte(s) of the alloys or mixtures.

[0022] Reaction of metallic precursors comprising Cu, In and Ga, with Group VIA materials may be achieved various ways. In one case the precursor layer is exposed to Group VIA vapors at elevated temperatures. These techniques are well known in the field and they involve heating the precursor layer 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 case a layer or multi layers of Group VIA materials are deposited on the precursor layer and the stacked layers are 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 precursor layer. Alternately inks comprising Group VIA nano particles may be prepared and these inks may be deposited on the 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 60 minutes depending upon the temperature. As a result of reaction, the Group IBIIIAVIA compound layer doped with an alkali metal is formed on the base.

[0023] It should be noted that the method of the present invention is also applicable to a precursor stack comprising an electroplated layer of a Group VIA material. For the example of Se as the Group VIA material, such all-electroplated stacks include but are not limited to Cu/Ga/In/Se, Cu/Ga/Cu/In/Se, Ga/Cu/In/Se, In/Cu/Ga/Se, Cu/In/Ga/Se, In/Cu/Ga/Cu/Se, In/Cu/Ga/In/Se, In/Cu/In/Ga/Se, In/Cu/Ga/In/Cu/Se, In/Cu/In/Ga/Cu/Se, Ga/Cu/In/Cu/Se, Ga/Cu/In/Ga/Se, Ga/Cu/Ga/In/Se, Ga/Cu/In/Ga/Cu/Se, Ga/Cu/Ga/In/Cu/Se, Ga/In/Cu/Se, Ga/In/Cu/Ga/Se, Ga/In/Cu/In/Se, Ga/In/Cu/Ga/Cu/Se, Ga/In/Cu/In/Cu/Se, Ga/In/Ga/Cu/Se, In/Ga/Cu/Se, In/Ga/Cu/In/Se, In/Ga/Cu/Ga/Cu/Se, and In/Ga/Cu/In/Cu/Se stacks wherein all of In, Ga, Cu and Se layers are electroplated. In this case, for doping the CIGS absorbers by reacting such stacks at elevated temperatures, it is preferred that all the plating electrolytes used for plating Cu, In, Ga and Se layers contain an alkali metal such as Na, preferably at a concentration in the range of 500 ppm-2M.

[0024] In the present invention the alkali metal is included in a metallic stack comprising Cu, In and Ga or in a precursor layer comprising Cu, In, Ga and a Group VIA material such as Se. The precursor layer or the metallic stack does not contain any appreciable amount of the Group IBIIIAVIA compound. Only after a high temperature reaction step, Cu, In, Ga and Group VIA material react with each other and form the Group IBIIIAVIA compound layer. Electroplating the Group IBIIIAVIA compound directly on a contact layer out of electrolytes comprising alkali metals does not yield good doping efficiency because the compound is already formed during the electroplating step. Including the alkali metal into the unreacted or partially reacted metallic stacks or precursors during electroplating yields better doping efficiency in the Group IBIIIAVIA compound layer formed as a result of a reaction step carried out after electroplating. Also inclusion of alkali metal in a metallic stack or precursor layer may be more and more efficient if the metallic stack or the precursor layer comprises more and more sub-layers. This is because alkali metals such as Na can be included more easily in small grain materials at interfaces between layers. Therefore, an electroplated stack that contains more sub-layers (such as a Cu/Ga/Cu/In stack) may contain more Na than a stack that contains less number of sub-layers (such as a Cu/In stack).

[0025] Solar cells may be fabricated on the 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 such as 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.

[0026] Although the present invention is described with respect to certain preferred embodiments, modifications thereto will be apparent to those skilled in the art.

1. A method of preparing a doped Group IBIIIAVIA absorber layer for a solar cell, the method comprising:

forming a metallic stack, the step of forming the metallic stack including the steps of:

electroplating at least one layer of a Group IB material using one or more Group IB plating solutions, and

electrodepositing at least one layer of a Group IIIA material using one or more Group IIIA plating solutions; and

reacting the metallic stack with at least one Group VIA material,

wherein the one or more Group IB plating solutions and the one or more Group IIIA plating solutions each contain a concentration of an alkali metal selected from the group of Na, K and Li.

2. The method according to claim 1 wherein the Group IB material is Cu, at least one layer of the Group IIIA material is a plurality of layers including an In layer and a Ga layer.

3. The method according to claim 2 wherein the steps of electroplating and electrodepositing form a metallic stack selected from the group of Cu/Ga/In, Cu/Ga/Cu/In, Ga/Cu/In, In/Cu/Ga, Cu/In/Ga, In/Cu/Ga/Cu, In/Cu/Ga/In, In/Cu/In/Ga, In/Cu/Ga/In/Cu, In/Cu/In/Ga/Cu, Ga/Cu/In/Cu, Ga/Cu/In/Ga, Ga/Cu/Ga/In, Ga/Cu/In/Ga/Cu, Ga/Cu/Ga/In/Cu, Ga/In/Cu, Ga/In/Cu/Ga, Ga/In/Cu/In, Ga/In/Cu/Ga/Cu, Ga/In/Cu/In/Cu, Ga/In/Ga/Cu, In/Ga/Cu, In/Ga/Cu/In, In/Ga/Cu/Ga/Cu, and In/Ga/Cu/In/Cu.

4. The method according to claim 3 wherein the concentration of the alkali metal is in the range of 500 ppm-2M.

5. The method according to claim 1 further comprising a step of electrodepositing a layer of Se using a Se plating solution on the metallic stack thus forming a precursor layer.

6. The method according to claim 5 wherein the Se plating solution comprises an amount of an alkali metal selected from the group of Na, K and Li.

7. The method according to claim 6 wherein the amount of the alkali metal is in the range of 500 ppm-2M.

8. The method according to claim 1 wherein the metallic stack contains at least 10^{19} atoms/cc of the alkali metal.

9. The method according to claim 6 wherein the precursor layer contains at least 10^{19} atoms/cc of the alkali metal.

10. A method of preparing a doped Group IBIIIAVIA absorber layer for a solar cell, the method comprising:

forming a metallic stack, the step of forming the metallic stack including the steps of:

electroplating at least one metallic layer including Cu and at least one of Ga and In using a first plating solution, and

electrodepositing at least one film including at least one of Ga and In using a second plating solution; and

reacting the metallic stack with at least one Group VIA material,

wherein the first plating solution and the second plating solution each contains a concentration of an alkali metal selected from the group of Na, K and Li.

11. The method according to claim 10 wherein the concentration of the alkali metal is in the range of 500 ppm-2M.

12. The method according to claim 10 further comprising a step of electrodepositing a layer of Se using a Se plating solution on the metallic stack thus forming a precursor layer.

13. The method according to claim 12 wherein the Se plating solution includes an amount of an alkali metal selected from the group of Na, K and Li.

14. The method according to claim 13 wherein the amount of the alkali metal is in the range of 500 ppm-2M.

15. The method according to claim 13 wherein the precursor layer contains at least 10^{19} atoms/cc of the alkali metal.

16. The method according to claim 10 wherein the metallic stack contains at least 10^{19} atoms/cc of the alkali metal.

* * * * *