The present inventions relate to selenium containing electrodeposition solutions used to manufacture solar cell absorber layers. In one aspect is described an electrodeposition solution to electrodeposit a Group IB-Group VIA thin film that includes a solvent; a Group IB material source; a Group VIA material source; and at least one complexing that forms a complex ion of the Group IB material. Also described are methods of electroplating using electrodeposition solutions.
SELENIUM CONTAINING ELECTRODEPOSITION SOLUTION AND METHODS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is a Continuation in Part of U.S. patent application Ser. No. 12/121,687 filed May 15, 2008 entitled “SELENIUM ELECTROPLATING CHEMISTRIES AND METHODS” (SP-049), and this application is a Continuation in Part of U.S. patent application Ser. No. 12/371,546 filed Feb. 13, 2009 entitled “ELECTROPLATING METHODS AND CHEMISTRIES FOR DEPOSITION OF COPPER-INDIUM-GALLIUM CONTAINING THIN FILMS” (SP-051P), and this application is a Continuation in Part of U.S. patent application Ser. No. 12/____ filed on Dec. 18, 2009 entitled “ENHANCED PLATING CHEMISTRIES AND METHODS FOR PREPARATION OF GROUP IIIVIA THIN FILM SOLAR ABSORBERS” (SP-098) and this application is a Continuation in Part of U.S. patent application Ser. No. 12/____ filed on Dec. 18, 2009 entitled “ELECTROPLATING METHODS AND CHEMISTRIES FOR DEPOSITION OF COPPER-INDIUM-GALLIUM CONTAINING THIN FILMS”, (SP-101), all of which are expressly incorporated herein by reference.

BACKGROUND

[0002] 1. Field of the Inventions

[0003] The present inventions relate to selenium containing electrodeposition solutions used to manufacture solar cell absorber layers.

[0004] 2. Description of the Related Art

[0005] 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 the 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.

[0006] Group IIIVIA 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(Si, or Cu(In, Ga)(S, Se)2 or CuIn1−x,Gax(S, Se)2 where 0≤x≤1, 0≤y≤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. It should be noted that although the chemical formula for CIGS (S) is often written as Cu(In,Ga)(S,Se)2, a more accurate formula for the compound is Cu(In(Ga)(S,Se)2, 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 structure of a conventional Group IBIIIVA compound photovoltaic cell such as a Cu(In,Ga),(S,Se)2 thin film solar cell is shown in FIG. 1. A photovoltaic cell 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. An absorber film 12, which comprises a material in the family of Cu(In,Ga),(S,Se), is grown over a conductive layer 13 or contact layer, which is previously deposited on the substrate 11 and which acts as the electrical contact to the device. The substrate 11 and the conductive layer 13 form a base 20 on which the absorber film 12 is formed. Various conductive layers comprising Mo, Ta, W, Ti, and their nitrides 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 the 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, CdS/ZnO or CdS/ZnO:ITO stack is formed on the absorber film 12. 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 Cu(In,Ga),(S,Se), 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.

[0008] The first technique that yielded high-quality Cu(In, Ga)Se2 films for solar cell fabrication was co-evaporation of Cu, In, Ga and Se onto a heated substrate in a vacuum chamber. However, low materials utilization, high cost of equipment, difficulties faced in large area deposition and relatively low throughput are some of the challenges faced in commercialization of the co-evaporation approach. Another technique for growing Cu(In,Ga),(S,Se)2 type compound thin films for solar cell applications is a two-stage process where metallic 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 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 CuIn(S,Se)2 layer can be grown.
Addition of Ga in the precursor layer, i.e. use of a stack such as a Cu/In/Ga stacked film precursor, allows the growth of a Cu(In,Ga)(S,Se)₂ absorber.

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 CuInSe₂ growth, for example, Cu and In layers are sequentially sputter-deposited on a substrate and then the stacked film is heated in the presence of gas containing Se at elevated temperatures 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 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.

Two-stage processing approach may also employ stacked layers comprising Group VIA materials. For example, a Cu(In,Ga)Se₂ or CIGS film may be obtained by depositing In—Ga—selenide and Cu—selenide layers in a stacked manner and reacting them in presence of Se. Similarly, stacks comprising Group VIA materials and metallic components may also be used. In—Ga—selenide/Cu stack, for example, may be reacted in presence of Se to form CIGS. Stacks comprising metallic elements as well as Group VIA materials in discrete layers may also be used. Selenium may be deposited on a metallic precursor film comprising Cu, In, and/or Ga through various approaches to form stacks such as Cu/In/Ga/Se and Cu—Ga/In/Se. One approach for Se layer formation is vapor deposition as described by J. Palm et al. (“CIS module pilot processing applying concurrent rapid selenization and sulfurization of large area thin film precursors”, Thin Solid Films, vol. 241-242, p. 514, 2003) in their work that involved preparation of a Cu—Ga/In metallic precursor film by sputtering and evaporation of Se over the In surface to form a Cu—Ga/In/Se stack. After rapid thermal annealing and reaction with S, these researchers reported formation of Cu(In,Ga)(S,Se)₂ or CIGS(S) absorber layer.

Evaporation is a relatively high cost technique to employ in large scale manufacturing of absorbers intended for high cost solar cell fabrication. Potentially lower cost techniques such as electroplating have been reported for deposition of Se films. Electroplating can be used for depositing substantially pure Se thin films as well as for co-depositing Se with Cu, In, and Cu metallic components. One specific method for the former case involves depositing a metallic precursor comprising Cu and In on a substrate and then electroplating a Se layer over the Cu and In containing layer to form a Cu—In/Se stack. This stack may then be heated up to form a CuInSe₂ compound absorber.

Binary metal selenide film preparation by electrodeposition has been reported in various publications. For example, Massacesi et al. carried out In—Se electroplating from indium sulfate and selenium acid solutions (“Electrodeposition of indium selenide In₅Se₃”, J. Electroanalytical Chemistry, vol. 412, p. 95, 1996). Kemell et al. (“Electrochemical quartz crystal microbalance study of the electrodeposition mechanism of Cu₅–Se thin film”, Electrochemical Acta, vol. 45, p. 3737, 2000) used a thiocyanate solution to deposit copper selenide thin films. In addition to preparation of substantially pure selenium films and binary metal selenides, one-step electroplating process has also been used to deposit the entire precursor film in the form of Cu—In—Se or Cu—In—Ga—Se. For example, CIGS films have been prepared with electrochemical co-deposition method from acidic solutions containing CuCl₂, InCl₃, GaCl₃, and SeO₂ (U.S. Pat. No. 6,872,295). The electrochemical co-deposition of CIS films is also performed using a solution containing Cu⁺⁺, In⁺⁺, Ga⁺⁺, and citrate salts, as reported in the literature (Olivera et al., “A voltammetric study of the electrodeposition of CuInSe₂ in a citrate electrolyte”, Thin Solid Films, vol. 406, p. 129, 2002).

Electrochemical deposition techniques have been developed to deposit pure Se films in both amorphous and metallic crystalline forms. Selenium can assume four allotropes modifications in its solid state: amorphous (also called vitreous), monoclinic and a hexagonal (so-called metallic) phase. The amorphous selenium is composed of irregular arrays of selenium chain molecules, while the monoclinic modifications consist of Se ring molecules. Vitreous and monoclonic modifications of Se are insulators and they are generally red in color. The hexagonal phase of selenium is gray in appearance and therefore called “gray” selenium. Hexagonal modification is a semiconductor due to the ordered arrangement of selenium chains facilitating electronic conduction. A. Von H alph et al. (U.S. Pat. No. 2,649,409) disclosed that gray crystalline metallic Se may be electroplated using an acidic electrolyte composed of saturated selenium dioxide in 9 molar H₂SO₄ at a temperature of 100°C. Since plating of metallic Se requires use of high temperature solutions and highly acidic solution formulations, they are not very suitable for large scale production.

Typically Se deposits obtained from low temperature solutions are of amorphous nature. A. Graham et al. (“Electrodeposition of amorphous Se”, J. Electrochemical Society., vol. 106, p. 551, 1959) have established that amorphous Se layers with thicknesses up to 500 nm can be plated using acidic (pH 0.7-0.9) or alkaline (pH 7.5-8.0) electrolytes in the temperature range between 20 to 40°C. A common problem associated with electrodeposition of amorphous Se films is that the current plating processes are known to produce colloidal Se which is mostly produced near the cathode surface. These colloidal Se particles aggregate and get larger in size with time. The formation of Se particles is not only observed in electrodeposition of pure Se layers but also occurs electroplating of metal selenides such as In—Se, Ga—Se, Cu—Se, Cu—In—Se, Cu—Ga—Se etc. The generation of colloidal particles might also be present in plating applications where other group VIA elements such as tellurium and sulfur are electrodeposited either in the form of pure elemental layers or co-deposited with Se such as sulfur-tellurium layers, tellurium-selenium layers and sulfur-tellurium-selenium layers, or co-deposited with metals such as In, Cu and Ga, or co-deposited with Se and metals such as In, Cu and Ga.

From the foregoing, there is a need in the solar cell manufacturing industry, especially in thin film photovoltaics, for better Se-containing electrodeposition solutions to deposit high quality Se containing films.

SUMMARY OF THE INVENTION

The present invention relates to selenium containing electrodeposition solutions used to manufacture solar cell absorber layers, and methods of using the same.

In one aspect is described an electrodeposition solution to electrodeposits a Group IB-Group VIA than film, com-
prising: a solvent; a Group IB material source that dissolves in the solvent and provides a Group IB material; a Group VIA material source that dissolves in the solvent and provides a Group VIA material; and at least one complexing agent that forms a complex ion of the Group IB material wherein such complex ion dissolves in the solvent; an adhesion promoting agent; a corrosion inhibitor; and wherein the pH of the electrodeposition solution is in the range of 1-13.

[0018] In another aspect is described a method of electrodeposition comprising a Group IB material on a conductive layer, comprising: providing an electrodeposition solution comprising a solvent, a copper ion source, a selenium ion source, at least one complexing agent and at least one adhesion promoting agent, the adhesion promoting agent suppressing the formation of colloidal particles on the substrate and in the plating solution, wherein the electrodeposition solution has a pH value in the range of 1-13; contacting the electrodeposition solution with the surface of the conductive layer and anode; establishing a potential difference between the anode and the conductive layer; and electrodepositing the copper selenide film on the surface of the conductive layer.

[0019] In a further aspect is described a method of electrodeposition comprising a precursor layer on a conductive layer, comprising: electrodeposition a copper selenide film on the conductive layer using an electrodeposition solution, the electrodeposition solution comprising a copper ion source, a selenium ion source, at least one complexing agent, at least one adhesion promoting agent; and depositing a thin film including a Group IB material, at least one Group VIA material onto the copper selenide film, wherein the step of depositing uses a physical vapor deposition technique.

BRIEF DESCRIPTION OF THE DRAWING

[0020] These and other aspects and features of the present invention will become apparent to those of ordinary skill in the art upon review of the following description of specific embodiments of the invention in conjunction with the accompanying figures, wherein:

[0021] FIG. 1 is a schematic view of a prior art solar cell structure;
[0022] FIG. 2A is a schematic view of a precursor stack electrodeposited on a base; and
[0023] FIG. 2B is a schematic view of a CIGS absorber layer formed when the precursor stack shown in FIG. 2A is reacted.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0024] The preferred embodiment, as described herein, provide electrodeposition (also called electroplating or plating) solutions (also called baths or electrolyte) and methods to co-electrodeposit (also called electrodeposition or electroplate) or plate from now on) uniform, smooth, continuous and compositionally repeatable Group IB-Group VIA alloy or mixture films. The electrodeposition solution compositions and methods of the present invention suppresses or eliminate the formation of metal cations in the electrodeposition solution, thereby allowing electrodeposition of defect-free and highly adherent, low stress Group IB-Group VIA alloy or mixture thin films at a high deposition rate in both conformal and non-conformal fashions. Such films can be used in the preparation of Group IB-Group VIA compound semiconductors.

[0025] In one embodiment, for example, the Group IB material may be Cu and the Group VIA material may be Se to electrodeplate a copper selenide, Cu—Se film. Such Cu—Se films may be used to form one or more layers of a precursor stack of a Cu(In,Ga)(Se)₂ absorber layers. The stoichiometry or composition of such films, e.g. Group IB/Group VIA atomic ratio, may be controlled by varying the composition of the electrodeposition solution and by modification of the appropriate plating conditions. For example, the composition of Se in the deposited copper-selenide film may be tailored to a specific composition or varied in a desirable manner within the thickness of the film. The disclosed electrodeposition Cu—Se electrodeposition solutions may be used to deposit a copper selenide films containing more than, for example, 95% Se at pH values lower than 3 as well as deposit highly copper rich selenide at pH values higher than 7.5. Through the use of embodiments described herein it is possible to form micron or sub-micron thick Cu—Se films on conductive surfaces for the formation of solar cell absorbers.

[0026] The electrodeposition solution of the present invention comprises a Group IB material, such as a copper source, a source of Group VIA material such as a selenium source, at least one complexing agent, an adhesion promoting agent, a corrosion inhibitor such as multihydric alcohol, for example glycerol, a pH adjuster and a solvent such as water. The pH range of the plating solution is between 1 and 13. The pH of the plating bath can be modified, for example, depending on the nature of the substrate, the copper content of the copper selenide film.

[0027] A Cu—Se electrodeposition solution, or electrodeposition solution or solution hereinbelow, of the present invention includes known soluble copper salts, for example, sulfates, chlorides, nitrates, oxides, hydroxides, tetrafluoroborates, citrates, acetate gluconate, phosphates, sulfimates, carbonates, copper amine salts or the like as the Cu source. A copper sulfate source may preferably be used as the Cu source in this invention. Cu source may comprise stock solutions prepared by dissolving copper metal into its ionic form in a suitable solvent such as water. The copper ions concentration may be in the range of 1-500 mM/L and preferably 5-100 mM/L.

[0028] In the Cu—Se electrodeposition solution, selenium oxide may provide the Group VIA material source although other Group VIA compounds or elemental Group VIA materials may also be used for this function as long as they dissolve in the electrodeposition solution. In certain embodiments, the Group VIA material source may be compounds of Se, S, and Te such as acids of Se, S, and Te as well as oxides, chlorides, sulfates, nitrates, perchlorides, and phosphates of Se, S, and Te. The Se source may preferably include soluble selenium salts or acid or combination of both, for example, sodium selenate and selenious acid. The selenium content in the Cu—Se electrodeposition solution may be in the range of 50-1.5 M/L, preferably 75-700 mM/L.

[0029] The Cu—Se electrodeposition solution may include at least one complexing agent. The complexing agents may be water soluble complexing agents with carboxylate and/or an amine group. A blend of two or more complexing agents can be included to provide full complexation of Group IB ions including Cu ions. Complexing agents can be selected from organic acids such as citric acid, tartaric acid, maleic acid, malic acid, oxalic acid succinic acid, ethylenediamine (EN), ethylenediaminetetraacetic acid (EDTA), nitrotriacetic acid (NTA), and hydroxyethylendiaminetriacetic acid
(HEDTA). The salts of these acids with alkali metals and alkali earth metals can be also used as the source for complexing agents. Sodium citrate, potassium tartrate and calcium oxalate can be used to provide citrate, tartrate and oxalate complexing ions, respectively. Ammonium salts of these complexing agents can be also used to provide the complexing ions. For example, ammonium citrate, either in the form of ammonium citrate dibasic or in the form of ammonium citrate trisulfate was found to be a very useful source material to provide citrate complexing ions in the electrodeposition solution. The complexing agent content of the electrodeposition solution may preferably be in the range of 5 mM/L to 0.55 M/L, more preferably between 0.1 M to 0.4 M/L. When ammonium citrate is used as the complexing agent source, the ammonium citrate content of the electrodeposition solution may vary between 0.05 M/L and 0.4 M/L, and preferably between 0.08 M/L and 0.35 M/L. It is also possible to prepare this electrodeposition solution for other Group IB materials. Silver (Ag) or gold (Au) ion sources may also be added to Cu—Se electrodeposition solutions to deposit layers including them. For example, in one embodiment, an electrodeposition solution including Cu, Ag and Se may be prepared to electrodeposited Cu—Ag—Se layers. In this case, an additional complexing agent Ag may or may not be added to the electrodeposition solution.

The electrodeposition solution of the present invention might further include other compounds, specifically added to increase the conductivity of the electrodeposition solution. The conductivity improving agents might be selected from ammonium salts of inorganic acids, alkali metal salts of inorganic acids, and alkali metal earth salts of inorganic acids. The conductivity improving agents might include but not limited to ammonium sulfate, potassium sulfate, sodium sulfate, magnesium sulfate, ammonium nitrate, potassium nitrate, sodium nitrate, magnesium nitrate, ammonium chloride, potassium chloride, sodium chloride, magnesium chloride. For example, ammonium sulfate was found to be a very useful source material to high conductivity in the bath. The conductivity improving agent content of the electrodeposition solution may preferably be in the range of 5 mM/L to 0.55 M/L, more preferably between 0.1 M to 0.4 M/L. When ammonium sulfate is used as the conductivity improving agent source, the ammonium sulfate content of the electrodeposition solution may vary between 0.05 M/L and 0.4 M/L, and preferably between 0.08 M/L and 0.35 M/L.

The adhesion promotion agent added to the Cu—Se electroplating solution enhances Cu—Se film formation and its adhesion to the surface of the underlying layer during the electrodeposition process. Adhesion promoting agents may be selected from a group of organic compounds with amine functional groups, which can form very strong chelation with copper ions. Preferably, organic compounds with amine functional groups, which also contain at least one aminopropyl group are desirable because of their ability to form very stable complexes with copper ions. An exemplary adhesion promoting agent preferably includes an organic amine molecule with at least one nitrogen atoms, and preferably with opposing multiple nitrogen atoms or nitrogen bearing group. For example, organic compounds with piperazine functional groups may be used as adhesion promoting agents in this invention. The adhesion promoting agents not only improve the adhesion of the film but also largely suppress the formation of powdery or colloidal Se particles or aggregates that might form on the cathode and within the electrolyte solution during the plating process. Therefore, they also provide a large increase in the cathodic efficiency for plated films. Examples of suitable adhesion promotion agents of this invention included but not limited to 1,4-Bis(3-aminopropyl) piperazine and N, N' Bis(3-aminopropyl) ethylenediamine. Alternatively, any possible mixture of these adhesion promoting agents may be used in the electrodeposition solution of the present invention. The amount of the adhesion promoting agents in the electrodeposition solution is in the range of 0.01 mM/L to 200 mM/L, preferably in the range of 1.0 mM/L to 40 mM/L.

Another key constituent of the Cu—Se electrodeposition solution is an organic compound, which acts as a corrosion inhibitor when electrodeposition is conducted on a galvanically more active surface, for example Cu—Se plating over In and Ga metal or alloy thin films comprising In and Ga metals or alloys comprising In and Ga. Such organic corrosion inhibitors of the present invention might be selected from multifunctional alcohols. Specifically, glycerol was found to be particularly useful for the Cu—Se electrodeposition solution. The addition of glycerol into the Cu—Se electrodeposition solution, suppresses/eliminates the dissolution or partial dissolution of some substrate thin film material during the electrodeposition step. The glycerol enhances substrate wetting and improves coating uniformity by dispersing any particulates in the solution as well as suppressing their adhesion to the substrate surface. When added at high concentrations, in the presence of adhesion promoting compounds with piperazine functional groups, glycerol may also refine the microstructure of the plated Cu—Se film, by forming smaller grains in a uniform fashion with a good surface coverage. The concentration of the multifunctional alcohols, such as glycerol in the present invention may vary between 20 mM/L to 500 mM/L and preferably between 30 mM/L to 250 mM/L.

The Cu—Se electroplating solution of the present invention might further include grain-refiners. To obtain a layer with a microstructure with finer grains, inorganic additives with chloride, pyrophosphate and sulfite ions might be added to the electrodeposition solution. The chloride additives may include known water soluble chloride compounds, for example, sodium chloride, ammonium chloride. The pyrophosphate additives may include for example potassium pyrophosphate. The sulfite additives may include sodium sulfite. It is also preferable that the concentration of the sulfite, or chloride, or pyrophosphate and their various combinations does not exceed 1% of the Cu—Se electrodeposition solution. Excessive amount of chlorides, pyrophosphates and sulfites might produce defective films and may lead to premature excessive selenium precipitation in the electrodeposition cell.

The Cu—Se electrodeposition solutions of present invention may be prepared in a wide range of pH value between 1 and 13. The specific pH of the electrodeposition solution depends on factors such as the nature of the substrate, level of conformity desired in the film, and the copper content of the copper selenide film. A pH range between 1 and 5, more preferably between 1.5 to 3, is suitable for plating operations to deposit Se rich Cu—Se films with a high Se/Cu ratio, greater than 10. In this acidic pH regime, the pH of the plating bath may be adjusted with a pH adjuster, which could be as simple as an inorganic acid such as sulfuric acid or sulfonic acid or a pH buffer couple chosen for the pH of the particular application. Increasing pH of the electrodeposition solution allows deposition of Cu—Se films with higher Cu content. A
highly Cu rich Cu—Se film may be deposited at pH values greater than 7.5. The pH of the solution in the alkaline regime can be adjusted by addition of sodium hydroxide, potassium hydroxide or ammonium hydroxide. Alkaline buffer couples could be also employed to adjust the pH. Such alkaline pH buffer systems include but not limited to monopotassium phosphate/dipotassium phosphate, boric acid/sodium hydroxide, sodium bicarbonate/sodium carbonate, monosodium tetraborate/disodium tetraborate, monosodium ascorbate/di- sodium ascorbate, and dipotassium phosphate/tripotassium phosphate. The pH value of the electrodeposition solution also regulates the formation of the Cu—Se film.

[0035] Electrodeposited Group IBVIA layers using the electrodeposition solution can be employed in the preparation of precursor layers in a two-stage process where such precursor layers are reacted in a high temperature annealing process. During reaction, sulfur and/or more selenium might present to produce the desired compound form. FIG. 2A shows an exemplary precursor stack 100 which will be utilized below to describe various uses of the electrodeposition solution of the present invention. In this embodiment, the precursor stack 100 may include a multilayer structure including a first layer 102, a second layer 104 and an optional third layer 106. In this embodiment, at least a portion of the precursor stack 100 is electrodeposited using the Cu—Se electrodeposition solution of the present invention. During the process, initially, the first layer 102 may be formed over a base 101 which may include a substrate 101A and a contact layer 101B formed over the substrate. The second layer 104 is electrodeposited on the first layer 102 and the third layer 106 may be electrodeposited on the second layer. Principles of the electrodeposition process are well known and will not be repeated here for the sake of clarity. The contact layer 101B may be made of a molybdenum (Mo) layer deposited over the substrate 101A or a multiple layers of metals stacked on a Mo layer, for example, molybdenum and ruthenium multilayer (Mo/Ru), or molybdenum, ruthenium and copper multilayer (Mo/Ru/Cu). To form a contact layer having multi layers, for example, Ru layer may be electrodeposited on the Mo layer, and similarly the Cu layer may be electrodeposited on the Ru layer to form the contact layer. The substrate 101A may be a flexible substrate, for example a stainless steel foil, or an aluminum foil, or a polymeric substrate. The substrate may also be a rigid and transparent substrate such as glass.

[0036] As shown in FIG. 2B, in the following step, the precursor stack 100 is reacted in a reactor to transform it to an absorber layer 108 i.e., a compound layer. As will be described below, the composition of the precursor stack determines the composition of the resulting absorber layer or compound layer. In one embodiment, the Cu—Se electrodeposition solution of the present invention may be used to prepare Group IBVIA compound semiconductors such as CuInSe₂, CuGaSe₂, CuAlSe₂, Cu(In, Ga)Se₂, Cu(In, Al, Ga)Se₂, Cu(In, Al, Ga)(Se, S)₂ and Cu(In, Ga)(Se, S)₂, which can be used as solar absorber layers. In this case, the first layer 102 and the second layer 104 of the precursor stack may comprise Group IB, Group IIIA and Group VIA materials, i.e., Cu, In, Ga and Se to form a Group IBVIA compound layer.

[0037] In this embodiment, the first layer 104 may be configured as a stack including a Cu-film, an In-film and a Ga-film, which will be shown with Cu/In/Ga insinuation hereinbelow. This and similar insinuations will be used throughout the application to depict various stack configurations, where the first material (element or alloy) symbol is the first film, the second material symbol is the second film deposited on the first film and so on. For example, in the Cu/In/Ga stack: the Cu-film, as being the first film of the stack, may be electrodeposited over the contact layer or another stack; the In-film (the second film) is electrodeposited onto the Cu-film; and the Ga-film (the third film) is deposited onto the In-film. In the first layer 102, the order of such films 102 may be changed, and the first layer 102 may be formed as a Ga/Cu/In stack or In/Cu/Ga stack. Furthermore, the first layer 102 may be formed as a stack of four films, such as Cu/Ga/Cu/In or Cu/In/Cu/Ga. In another embodiment, the first layer 102 may be formed as a (Cu—In—Ga) ternary alloy film or as a stack including (Cu—In) binary alloy film and (Cu—Ga) binary alloy film. Such alloy binary or ternary alloy films may have any desired compositions. The first layer 102 may be formed by any possible combinations of the above given stacks of films, binary films and ternary alloy films.

[0038] Referring back to FIG. 2A, the second layer 104 includes a Cu—Se alloy film electrodeposited using the electrodeposition solution of the present invention. Alternatively, the second layer may include a mixture films including at least one of the films included in the first layer and at least one film of Cu—Se. The third layer 106 is an optional layer to add more Se to the precursor stack 100. If more Se is desired in the precursor, it could be added as the third layer 106. Preferably, the second layer includes a Cu—Se film.

[0039] Alternatively, the Cu—Se electrodeposition solution of the present invention may be used to form precursors for absorber layers comprising ternary compounds such as CuGaSe₂, CuInSe₂, CuAlSe₂. In this embodiment, the first layer 102 may comprise a Group IIIA material, such as one of In, Ga, or Al, and the second layer 104 comprises (Cu—Se) film. Precursor stacks including Ga/(Cu—Se), In/(Cu—Se) and Al/(Cu—Se) can be prepared by electrodepositing the (Cu—Se) layer over Ga, In and Al films, respectively, which are deposited on, for example, a contact layer such as Mo. Such layers can be later reacted at high temperature in a S and/or additional Se-containing environment to form CuGaSe₂, CuInSe₂, CuAlSe₂, respectively.

[0040] The copper selenide (Cu—Se) film of the present invention may be deposited at very high deposition rates. The electrodeposition current density may be greater than 30 mA/cm² as compared to typical 2 mA/cm² of the prior art. Cu—Se film is very uniform and exhibits excellent adhesion and around pH=2. The Cu—Se film composition is independent of plating current density between 5 and 30 mA/cm². The copper content of the Cu—Se film may be varied between less than 6% and more than 50% by, for example: adjusting pH alone; adjusting copper content of the Cu—Se electrodeposition solution; adjusting selenium content of bath; and the addition of sulfonic acid or EDTA. The Cu—Se electrodeposition solution is capable of electrodepositing a film including very high Se content. For example, the Cu—Se electrodeposition solution can deposit copper selenide films with less than 6% copper on indium substrates with minimal indium loss. For copper rich continuous and adherent Cu—Se films, the selenous acid may be replace with sodium selenate and Cu—Se films plated at pH between 7 and 13, and preferably at a pH between 8 and 11.

**EXAMPLE**

[0041] An exemplary Cu—Se electrodeposition solution was prepared and electrodeposited on a thin film of In with
approximately 3000 Angstrom thickness, which was electroplated over a Mo/Cu containing stack on stainless steel substrate. The Cu—Se electrodeposition solution includes the following composition: 5 g/L copper sulfate pentahydrate; 30 g/L sodium citrate; 60 g/L sodium sulfate; and 50 g/L selenium acid. The pH of the electrodeposition solution was adjusted to 2 by adding sulfuric acid. During the electrodeposition, a potential difference is established between the metallic surface and an anode such as Pt coated Ti electrode. A plating current density of about 30 mA/cm² is applied for 60 seconds. The electrodeposition process resulted in a Cu—Se film having a thickness of about 330 nm. Generation of Se particles or aggregates was observed emanating from the cathode surface during the deposition step. In the following experiment, the addition of 1.25 ml/liter 1,4-Bis(3-aminopropyl) piperazin as the adhesion promoting agent to this electrodeposition solution produced an extremely adherent film and no visible Se particle or aggregate generation during the plating process. This provided a large increase in the cathodic efficiency yielding a thickness of 562 nm.

[0042] The Cu—Se electrodeposition solutions may also be used to form graded Cu—Se films, or to vary the copper composition profile, within the film thickness, by varying electrodeposition current density during the electrodeposition. The plating current density may be graded from a high current density and terminated with a much lower current density or vice versa. The much lower current density Cu—Se film containing comparatively higher copper percentage than the film plated at higher current density. The current may be pulsed between a higher and a lower current density for desirable time intervals to coat a laminated selenide films containing with different copper concentrations. For example, at a fixed pH, a Cu—Se layer may be deposited at 25 mA/sq.cm for 60 s, the current density is reduced to 2.5 mA/sq.cm for 30 s. The selenide film deposited at 25 mA/sq.cm may contain about 8% copper and the film deposited at 2.0 mA/sq.cm may contain about 14% copper in the layer, producing a Cu—Se alloy with a copper rich surface. The laminate may be symmetrical or assymmetrical, the initial alloy coating may be relatively copper rich or copper poor with respect to the subsequent Cu—Se material coated.

[0043] The Cu—Se electrodeposition solution may be adapted for multi-cell operations, where individual cell may dispose variant chemistries of the Cu—Se electrodeposition solution. Such multi-cell plating approach may be used to vary the copper composition profile within the coating thickness. The substrate may be plated sequentially or non-sequentially across the various plating cells to achieved the desired alloy profile. The deposited Cu—Se films exhibit low stress characteristics. For example, more than 3 micron Cu—Se film may be electrodeposited on an indium film without film cracking or any local delamination. The Cu—S alloy films of this invention may be plated galvanostatically, the said alloys may also be deposited potentiostatically or various combinations of current and voltage mode.

[0044] The Cu—Se film of the present invention may be used to replace a significant portion of the evaporated selenium in the precursor, resulting in a very significant reduction in the operating cost of selenium evaporators. In another embodiment of this invention, the electrodeposited Cu—Se film may be covered or coated with other thin film materials, for example, sodium fluoride, indium, gallium, binary or ternary photovoltaic alloy material using PVD deposition techniques prior to the selenization step. As mentioned before, the Group IB material may also include silver (Ag) or gold (Au). For example

[0045] Although the present invention is described with respect to certain preferred embodiments, modifications thereto will be apparent to those skilled in the art.

We claim:

1. An electrodeposition solution to electrodeposits a Group IB—VIA thin film, comprising:
   a. a solvent;
   b. a Group IB material source that dissolves in the solvent and provides a Group IB material;
   c. a Group VIA material source that dissolves in the solvent and provides a Group VIA material; and
   at least one complexing agent that forms a complex ion of the Group IB material wherein such complex ion dissolves in the solvent;
   an adhesion promoting agent;
   a corrosion inhibitor; and
   wherein the pH of the electrodeposition solution is in the range of 1-13.

2. The electrodeposition solution of claim 1, wherein the Group IB material source comprises a copper source and the Group VIA material comprises a selenium source.

3. The electrodeposition solution of claim 2, wherein the copper source of copper ions comprises at least one of dissolved copper metals and dissolved copper salts, wherein the copper salts include copper-chloride, copper-sulfate, copper-acetate, copper-oxide, copper-hydroxide, copper-nitrate, copper-phosphate, copper-tetrafluoroborate, copper-citrinate, copper-gluconate, copper-sulfamate, and copper-carbonate.

4. The solution of claim 1, wherein the Group Se material source comprises at least one of dissolved elemental Se, acids of Se, and dissolved Se compounds, wherein the Se compounds include oxides, chlorides, sulfates, nitrates, perchlorides and phosphates of Se.

5. The solution of claim 4 wherein the complexing agent includes at least one of a carboxylic functional group and an amine functional group.

6. The solution of claim 5 wherein the complexing agent comprises one of an acid and an alkali metal salt of the acid and an ammonium salt of the acid, and wherein the acid comprises one of tartaric acid, citric acid, acetic acid, malonic acid, malic acid, succinic acid, ethylenediamine (EN), ethylenediamine tetraacetic acid (EDTA), nitritolatriacetic acid (NTA), and hydroxyethyltriamine tetraacetic acid (HEDTA).

7. The solution of claim 6 wherein the complexing agent comprises an alkali metal salt of the acid is selected from the group of sodium and potassium salts tartaric acid, citric acid, acetic acid, malonic acid, malic acid, succinic acid, ethylenediamine (EN), ethylenediamine tetraacetic acid (EDTA), nitritolatriacetic acid (NTA), and hydroxyethyltriamine tetraacetic acid (HEDTA).

8. The solution of claim 6 wherein the complexing agent comprises an ammonium salt of the acid is selected from the group of ammonium salts of tartaric acid, citric acid, acetic acid, malonic acid, malic acid, succinic acid, ethylenediamine (EN), ethylenediamine tetraacetic acid (EDTA), nitritolatriacetic acid (NTA), and hydroxyethyltriamine tetraacetic acid (HEDTA).

9. The electrodeposition solution of claim 4, wherein the amount of the complexing agent is in the range of 5 mM/L to 0.55 M/L.
10. The electrodeposition solution of claim 1, wherein the adhesion promoting agent comprises organic compounds with at least one amine functional group and at least one aminopropyl group.

11. The electrodeposition solution of claim 11, wherein the adhesion promoting agent comprises at least one of 1,4-Bis (3-aminopropyl) piperazine and N,N'-Bis(3-aminopropyl) ethylenediamine and any possible mixture of these.

12. The electrodeposition solution of claim 7, wherein the amount of the adhesion promoting agent is in the range of 1.0 mM/L to 40 mM/L.

13. The electrodeposition solution of claim 1, wherein the corrosion inhibitor comprises a multihydric alcohol.

14. The electrodeposition solution of claim 13, wherein the corrosion inhibitor is glycerol.

15. The electrodeposition solution of claim 13, wherein the amount of the corrosion inhibitor is in the range of 20 mM/L to 500 mM/L.

16. The electrodeposition solution of claim 1 further comprising a grain refiner including one of chloride, pyrophosphate and sulfite.

17. The electrodeposition solution of claim 1 further comprising a conductivity improving agent including ammonium sulfate.

18. The electrodeposition solution of claim 1, wherein the amount of the conductivity improving agent is in the range of 5 mM/L to 0.55 M/L.

19. A method of electrodepositing an adherent film comprising copper selenide alloy material on a conductive layer, comprising:

- providing an electrodeposition solution comprising a solvent, a copper ion source, a selenium ion source, at least one complexing agent and at least one adhesion promoting agent, the adhesion promoting agent suppressing the formation of colloidal particles on the substrate and in the plating solution, wherein the electrodeposition solution has a pH value in the range of 1-13;
- contacting the electrodeposition solution with the surface of the conductive layer and an anode;
- establishing a potential difference between the anode and the conductive layer; and
- electrodepositing the copper selenide film on the surface of the conductive layer.

20. The method of claim 19, wherein the conductive layer is one of indium, gallium, selenium copper and their alloys.

21. The method of claim 19 where in the copper ion source is copper sulfate pentahydrate, and the selenium ion source is selenium oxide.

22. The method of claim 19, wherein said adhesion promoting agent comprises organic compounds with at least one amine functional group and at least one aminopropyl group.

23. The method of claim 19, wherein the step of electrodepositing includes varying electrodeposition current density during the electrodeposition.

24. The method of claim 19, wherein the step of electrodepositing includes pulsing the current density between a high and a low current density for desirable time intervals to electrodeposit laminated selenide films containing different copper concentrations.

25. The method of claim 19 wherein said copper selenide film has a graded copper composition within the film thickness.

26. The method of claim 19 wherein the step of electrodepositing is performed using one of galvanostatic electrodeposition, potentiostatic electrodeposition, and various combinations of current and voltage mode.

27. A method of electrodepositing a precursor on a conductive layer, comprising:

- electrodepositing a copper selenide film on the conductive layer using an electrodeposition solution, the electrodeposition solution comprising a copper ion source, a selenium ion source, at least one complexing agent, at least one adhesion promoting agent; depositing a thin film including a Group IB material, at least one Group IIIA material onto the copper selenide film, wherein the step of depositing uses a physical vapor deposition technique.

28. The method of claim 27 wherein the thin film further includes a sodium salt.

29. The method of claim 27 wherein the Group IB material includes copper, and the Group IIIA material includes gallium and indium.

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