INDIUM ELECTROPLATING BATHS FOR THIN LAYER DEPOSITION

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Abstract

Indium (In) electroplating solutions which are used to deposit compositionally pure, uniform, substantially defect free and smooth In films with near 100% plating efficiency and repeatability. In one embodiment the plating solution includes an In source, citric acid and its conjugate pair salt and a solvent. At a pH value of below 4.0, sub-micron thick In layers with close to 100% purity at close to 100% plating efficiency are produced. Such In layers are used in fabrication of electronic devices such as thin film solar cells.
INDIUM ELECTROPLATING BATHS FOR THIN LAYER DEPOSITION

BACKGROUND OF THE INVENTION

[0001] 1. Field
[0002] This invention relates to indium (In) electroplating methods and chemistries to deposit uniform, defect-free and smooth In thin films with high plating efficiency and repeatability. These In thin films may be used in fabrication of electronic and semiconductor devices such as thin film solar cells.

[0003] 2. Description of the Related Art
[0004] Indium (In) is an important metal used in semiconductor and electronics industries. Indium is generally recovered as a by-product from zinc and lead-zinc production. Electrodeposition is a common method to recover bulk In. A number of In electroplating baths have also been formulated to deposit layers of In on various conductive substrates. For example, In plating baths containing sulfamate (U.S. Pat. No. 2,458,839), cyanide (U.S. Pat. No. 2,497,988), alkali hydroxides (U.S. Pat. No. 2,287,948), tartaric acid (U.S. Pat. No. 2,423,624), and fluoborate (U.S. Pat. No. 3,812,020, U.S. Pat. No. 2,409,983) have been developed and commercialized. Some details on such chemistries may be found in the review paper of Walsh and Gabe (Surface Technology, vol: 8, pages: 87-99, 1979). In addition to the common aqueous In solutions, In can also be plated from organic solvent based solutions such as formamide (U.S. Pat. No. 2,452,361). Some of the In alloys that can be electroplated include indium–silver (U.S. Pat. No. 1,955,630), indium–tin (U.S. Pat. No. 6,331,240) and indium–nickel (U.S. Pat. No. 4,626,324, U.S. Pat. No. 4,686,015). Although it is possible to deposit In and In alloy layers using various prior art plating chemistries, such layers may not be suitable for preparation of smooth, uniform, defect-free In films with sub-micron thickness that are needed for thin film solar cell applications. Common defects in electroplated In layers include holes, or pinholes as will be described later.

[0005] One recent application of electroplated In films is in formation of Cu(In,Ga)(Se,S) or CIGS(S) films which are the most advanced compound absorbers for polycrystalline thin film solar cells. A thin In layer, for example, may be electroplated on a Cu layer. The Cu/In precursor stack thus obtained may then be reacted with Se to form a CuInSe2 or CIS absorber. Reaction with S would form a CIS(S) layer. For CIGS or CIGS(S) formation Ga is also included in the precursor stack. The CIGS(S) absorber may be used in fabrication of thin film solar cells with a structure of “contact/CIGS (S)/buffer layer/TCO”, where contact is a metallic layer such as a Mo layer, the buffer layer is a thin transparent film such as a CdS film and TCO is a transparent conductive oxide layer such as a SnO and/or ITO layer.

[0006] In a thin film solar cell employing a Group IIIA-VIA compound absorber such as CIS or CIGS, the cell efficiency is a strong function of the molar ratio of IIIA/IIIA. If there are more than one Group IIIA materials in the composition, the relative amounts or molar ratios of these IIIA elements also affect the properties. For a Cu(In,Ga)(S,Se)2 or CIGS(S) absorber layer, for example, the efficiency of the device is a function of the molar ratio of Cu/(In+Ga). Furthermore, some of the important parameters of the cell, such as its open circuit voltage, short circuit current and fill factor vary with the molar ratio of the IIIA elements, i.e. the Ga/(Ga+In) molar ratio. In general, for good device performance Cu/(In+Ga) molar ratio is kept at or below 1.0. For ratios close to or higher than 1.0, a low resistance copper selenide phase may form, which may introduce electrical shorts within the solar cells. As the Ga/(Ga+In) molar ratio increases, on the other hand, the optical bandgap of the absorber layer increases and therefore the open circuit voltage of the solar cell increases while the short circuit current typically may decrease. It is important for a thin film deposition process to have the capability of controlling both the molar ratio of III/VIIIA, and the molar ratios of the Group IIIA components in the composition. Therefore, if electrodeposition is used to introduce the In into the film composition, it is essential that the electroplated In films have smooth morphology and be free of defects such as pinholes. It should be appreciated that any protrusions in the In film will cause an In-rich region in the CIGS(S) absorber obtained after reaction with Se and/or S. Alternately, any pinholes or regions with thinner In would yield Cu-rich or In-poor regions which, after reaction with Se and/or S would turn into copper selenide-rich regions with low resistance, which would introduce electrical shunt between the contact layer and TCO layer of the solar cell, reducing the conversion efficiency of the device. Such non-uniform layers cannot be used for high efficiency solar cell manufacturing.

[0007] One other factor that is also important for manufacturing devices such as solar cells utilizing electroplating technique is the necessity for high electroplating efficiency and for stability of this efficiency as a function of time. Since electroplated In layer thickness depends directly on the plating efficiency and since the In layer thickness determines the Cu/(In+Ga) and Ga/(In+Ga) ratios which are crucial for CIGS(S) type solar cell operation, controlling and increasing the plating efficiency improves manufacturability and it also increases throughput of CIGS(S) absorber formation processes. The maximum cathode efficiency in the prior-art fluoborate In plating bath is only 75%. The In cyanide bath contains very toxic potassium cyanide and its cathode efficiency drops down with aging of the bath and thus In thickness changes with time. The alkaline hydroxide In plating baths may result in corrosion on the plated In surfaces and they usually need some additives to increase the stability and the deposition or plating efficiencies. Control of additives is difficult and costly in the manufacturing environment. As the most popular In electroplating bath, the In sulfamate plating solution generates In thin films with a cathode efficiency of about 90%. However, this bath requires some additives to improve the quality and morphology of the deposited layers. Organic additives may gradually decompose and start affecting deposit quality in a negative manner. They need to be monitored and replenished periodically and the bath needs to be totally replaced when a large concentration of decomposed additives accumulate in the solution. These are costly approaches and sulfamic acid and In-sulfamate salts are considerably expensive chemicals to be used in a low cost processing approach.

[0008] In most metal plating baths, the low plating efficiencies or cathode efficiencies are due to hydrogen generation. In high efficiency electrolytes hydrogen generation is reduced or eliminated. Hydrogen generation may not be very critical to most electroplating applications where low plating efficiency, high In film thickness control tolerance (+/-10% or more) and high defect density in the deposited layers may be tolerated. However, in semiconductor and electronic industries and especially in the above mentioned application of CIGS(S) solar cell manufacturing, low plating efficiency and associ-
ated generation of hydrogen bubbles become major problems. Hydrogen generated during a low efficiency electroplating process typically results in formation of pinholes on the plated thin films, mostly due to the formation of sub-micron or micron size hydrogen bubbles on the cathodic surface. These small bubbles typically stick to the cathode surface and restrict material deposition at those sites. As explained before, these sites without In or with less In compared to the other parts of the cathode surface later turn into Cu-rich regions in a finished CIGS absorber. Copper-rich regions, in turn, introduce low shunt resistance to solar cells and reduce their conversion efficiency. Furthermore, hydrogen generation is sensitive to the substrate or cathode surface conditions, which may change as a function of time and reduce the repeatability of producing pin-hole free In thin films. It should be noted that the typical thickness of In layers to be electroplated for CIGS(S) absorber formation is in the range of 100-500 nm.

[0009] Because In⁺⁺ cations precipitate as In(OH)₂ between pH values of about 4-12, complexing agents need to be used to get a clear In electroplating solution within this pH range. Some complexing agents, such as EDTA, cyanides, tartrates, have been employed for this purpose. However, the In electroplating baths containing these complexing agents yielded low cathodic current efficiencies and required some organic additives to stabilize the solutions. It may be for this reason that complexing agents are not popular in commercial In plating baths.

[0010] Fouda et al. [Bull. Soc. Chim. Fr., vol: 2, page: 270-272, 1987] compared the process results of some In plating baths containing acetate, thioacetate, chlorate, iodide, sulphate, oxalate, acetamide and citrate. Unfortunately, some of the data in this publication appears to be inconsistent. For example, the authors refer to the cathode current efficiencies listed in Table 1 and state that “The effect of complexing agent is shown in table 1, all current efficiencies were quite low”. In Table 1 all the current efficiencies are low (in the range of 18-64%), except one using citrate that is listed as 100%. Obviously this is a typographic error in Table 1, especially since in the same table, the rate of deposition is listed as 0.17 mg/min for the 100% efficient bath at 2.5 mA/cm² current density whereas the acetamide bath with 64% plating efficiency at the same current density is shown to yield a rate of deposition of 0.33 mg/min, which is higher than 0.17 mg/min. It should be appreciated that this is impossible. If we adjust for this discrepancy, the citrate bath efficiency would be about 50%, which would be consistent with the statement of the authors that all efficiencies in Table 1 are low. One other possible explanation for the discrepancy may be the fact that the solution with citrate yielded non-uniform and gray deposits. According to the authors, gray In deposits can be attributed to the deposition of double salts. In other words, the deposits may not be pure metallic In but may comprise In salts. In either case, it is clear from this publication that its authors could not obtain pure and uniform In films at high plating efficiency using the plating bath chemistries they listed.

[0011] As described by Fouda et al., the low cathodic current efficiencies might be attributed to the dilute In⁺⁺ concentration (0.02 M). It is possible that the authors kept this concentration low to avoid precipitation of In⁺⁺ species within the relatively high pH ranges they selected for formulations. Some of the baths in this study generated poor quality In deposits. For example, a bath with 0.5 M InCl₃ and 60 g/L of tri-sodium citrate (pH=5) yielded impure In deposits that were thick, non-uniform and gray, suggesting a powdery and granular deposit with rough morphology which possibly comprised salts as stated by the authors.

[0012] As can be seen from the foregoing discussion it is necessary to develop a new In electroplating bath with high cathodic efficiency that can provide high quality, smooth, substantially defect-free and pure electrodeposited In layers at low cost, which may be used in electronic and semiconductor applications such as in processing thin film solar cells.

SUMMARY OF THE INVENTION

[0013] The present invention relates to an In electroplating bath to deposit silvery white, uniform, substantially defect-free, smooth and pure metallic In films with high cathodic current efficiency and repeatability. Such layers may be used in fabrication of electronic devices such as thin film solar cells.

[0014] In certain embodiments, the present invention provides a plating solution or bath for application of an In layer on a conductive surface. The solution includes an In source, a weak acid and its conjugate pair salt, and a solvent, wherein the solution provides a sub-micron thick chemically pure In film on the conductor with a cathodic plating efficiency of about 95-100%, preferably an efficiency of 98-100%. The pH value of such solution is below about 4.0. In addition, the In plating bath of certain embodiments of the present invention features non-corrosive, environmentally green chemistry which is low cost and highly stable so that In layers with repeatable thickness and morphology may be electroplated employing simple maintenance of the bath in a manufacturing environment.

[0015] In another embodiment of the invention, the In plating solution has been applied to roll-to-roll electroplating to obtain an In containing film possessing a sub-micron thickness on the surface of a conductor in a large scale manufacturing line.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] FIG. 1 is a schematic illustration of an In layer electroplated on a conductive bottom layer.

DETAILED DESCRIPTION OF THE INVENTION

[0017] An embodiment of the invention provides an electroplating solution for application of a substantially pure indium (In) film onto a conductive surface at high plating efficiency, comprising a solvent, an In source providing In ions to the solvent with an In ion concentration of at least about 0.05 M, and a weak acid and a conjugate pair salt of the weak acid, wherein the pH value of the electroplating solution is below about 4.0. The solvent may optionally comprise water, and is preferably aqueous. The In source may be any suitable source of In ions and is preferably one or more of In-chloride, In-sulfate, In-acetate, In-carbonate, In-nitrate, In-perchlorate, In-phosphate, In-oxide and In-hydroxide. Exemplary weak acids which are suitable for this embodiment are citric acid, acetic acid, formic acid, thioacetic acid, glycolic acid, lactic acid, ascorbic acid, malic acid, butanoic acid, and pentanoic acid. In certain preferred embodiments the weak acid is citric acid. The conjugate pair salt of the weak acid may be any suitable salt and in preferred embodiments is a sodium, lithium, potassium, ammonium or alkyl (e.g., C₁-C₆ alkyl) ammonium salts of the weak acid. In certain
preferred embodiments where the weak acid is citric acid, the conjugate pair salt is one or more of sodium citrate, lithium citrate, potassium citrate, and a salt of an organically modified citrate, wherein the organically modified citrate comprises a citrate moiety such that one or more organic groups replaces (a) one or more hydrogens that are directly connected to a carbon or oxygen bonded to carbon 2 of the citrate moiety, or (b) the hydroxyl group bonded to carbon 2 of the citrate moiety.

[0018] Another embodiment of the invention provides a method of obtaining a substantially pure and substantially defect-free In film on a surface of a conductor comprising the steps of (i) providing a solution with a pH value below 4 wherein that solution comprises a solvent, an In source providing In ions to the solvent with an In ion concentration of at least 0.05 M, a weak acid and a conjugate pair salt of such weak acid; (ii) applying the solution onto an anode and the surface of the conductor, (iii) establishing a potential difference between the anode and the conductor, and (iv) electrodepositing the substantially pure In film on the surface of the conductor. In certain preferred embodiments the weak acid is citric acid and the conjugate pair salt is a citrate salt, preferably at least one of sodium citrate, lithium citrate, potassium citrate, and an organically modified citrate. In certain embodiments the In source includes one or more of In-chloride, In-sulfate, In-acetate, In-carbonate, In-nitrate, In-perchlorate, In-phosphate, In-oxide and In-hydroxide. In certain embodiments the temperature of the solution is within the range of 10-60°C. During the step of electrodeposition and preferably is controlled within such range prior to the step of electrodeposition.

[0019] The present invention provides a method to electroplate In films on conductive surfaces at close to 100% deposition efficiency and high repeatability. In one embodiment, the present invention may be used to manufacture Group III/V/III/VI/VIA compound solar cell absorbers including Group III (such as Ga and In), and Group VIA (such as Se and S) elements. To manufacture a solar cell absorber layer initially an absorber precursor layer must be formed over a base which may include a substrate and a contact layer formed on a surface of the substrate. FIG. 1 shows an absorber precursor structure 10 having a conductive bottom layer 12 and an In layer 14 electroplated on the conductive bottom layer 12 using the present invention. The conductive bottom layer 12 is formed on the base 16 which may comprise the substrate and the contact layer (not shown). The typical conductive bottom layers used in this invention may be copper (Cu) and gallium (Ga) layers. After electroplating the In film in accordance with the present invention, another element, e.g., selenium (Se), or Ga can be directly plated onto the resultant In layer to form multiple metal stacks. By electroplating an In film in a high efficiency manner on a Cu surface, for instance, the present invention may be used to manufacture Cu/In/Se, Cu/In/Ga/Se and other metallic stacks, which in turn may be employed in processing CIS or CIGS type solar cell absorbers.

[0020] The electrochemical methods have recently received more attention for CIGS film formation due to their potential low cost. For example, the CIGS films have been prepared with electrochemical co-deposition method from acidic solutions containing CuCl₂, InCl₃, GaCl₃ and SeO₂ (see for example, U.S. Pat. No. 6,872,295). The electrochemical co-deposition of CIS films was also performed from a solution containing Cu⁺², In⁺³, Se⁺⁴ and citrate salts, as reported in the literature (Oliveira et al., Thin Solid Films, vol: 405, p: 129-134, 2000). However, all these electrochemical co-plating or co-deposition methods have problems such as long plating times (about one hour), non-repeatable Cu/Group IIIA molar ratios, extremely low cathodic plating efficiencies, and defective films arising from hydrogen generation. Therefore, they have not been suitable for manufacturing and have only been conducted for academic purpose.

[0021] At the present time, the most practical industrial approach for growth of the CIS or CIGS thin films using electroplating is a "two-stage" process. In this process, controlled amounts of Cu, In, Ga and sometimes Se are electrodeposited in the form of Cu, In, Ga and Se containing thin film precursor stacks such as Cu-In/Ga-Se, Cu/Ga/In/Se, In/Cu/ Ga/In/Se, In/Cu/Ga/In/Se, In/Ga/Cu/In/Se, In/Ga/Cu/In/Se/Ga/In/Cu/In/Se, In/Ga/Cu/In/Se/Ga/In/Se/Ga/In/Cu/In/Se/Ga/In/Se/Ga, etc., on a base such as a substrate coated with a conductive contact layer. These stacks may then be annealed, or reacted, optionally with more Se, sulfur (S) or sodium (Na), to form a uniform thin film of the CIGS(S) alloy or compound on the contact layer. By controlling the thickness and morphology of the Cu, In, and Ga layers within the precursor stacks, the process yield in terms of compositional control may be improved compared to the above mentioned alloy plating approaches where two or more of the Cu, In, Ga, and Se species are co-deposited on the substrate.

[0022] As described above the control of the thickness and morphology of the deposited layers, such as the In layer, is extremely important. High yield and repeatability of a solar cell manufacturing process utilizing two-stage processing and electrodeposition of at least one of a Cu layer, an In layer and a Ga layer critically depend on the repeatability of the deposited thickness of the electroplated layers, from run to run. Furthermore, micro-scale compositional uniformity requires these electroplated films with sub-micron thickness to have smooth morphology with a surface roughness of typically less than 10% of the film thickness, and with desirable and controllable microstructure, which is typically a small-grain microstructure with sub-micron size grains. Stacks utilizing In films with rough surface morphology, for example, would result in the In content being changing locally, in micro-scale throughout the film although on the average the In content may be in the acceptable range. It should be noted that the typical acceptable CIGS(S) film composition has a Cu/(In+Ga) molar ratio in the 0.8-1.0 range whereas the Ga/(In+Ga) molar ratio may be in the range of 0.3-0.5.

[0023] With these thin film stacks, copper layers (or Ga layers) may be electroplated or sputter deposited on a base comprising a substrate which, on its surface, may have a conductive contact film such as a Mo layer and/or a ruthenium (Ru) containing layer. The substrate may be a metallic foil, glass or polymeric sheet or web. The Ru containing layer on the substrate surface may be a Ru layer, a Ru alloy layer, a Ru compound layer or a stack containing Ru such as a Mo/Ru stack or in general a M/Ru stack, where M is a conductor or semiconductor. Indium electroplating on the Cu surface (or the Ga surface) can be carried out at various current densities, such as at 5, 10, 20 and 30 mA/cm², using the electrolytes of the present invention. Both DC and/or variable (such as pulse or ramped) voltage/current waveforms may be utilized in electroplating the In layers.

[0024] In particular, this invention provides an efficient In plating bath employing weak acids and conjugates salts such as citrates. Films obtained using this solution are substantially
free from defects such as pinholes since hydrogen bubble formation on the cathode during plating is drastically reduced by the high plating efficiency. Electronic applications such as solar cells may tolerate a total pinhole area to be about 0.0001% of the total film area. Therefore, substantially pinhole-free means that on a 1 cm² size In-plated surface the total area of the pinholes (number of pinholes times the average size of pinholes) is less than about 10⁻⁴ cm².

Although citrates have been used in the In electrodeposition before, as described above, it did not provide pure and uniform layers. The optimized pH for the bath of the present invention is less than about 4, preferably less than about 3.5, more preferably less than 2.5, and most preferably the pH is about 2. Although there may be other explanations for the superior performance of the formulated bath, and without limiting the invention with respect to any particular theory, the following non-limiting points are observed with respect to the embodiment of the invention using citric acid and citrate. Present inventors realized that the citric acid (H₃Cit) has three pKₐ values. These are: pKₐ₁=3.06, pKₐ₂=4.74, and pKₐ₃=5.40, at 25°C. As a result of this, at a pH of 2, about 90% of the citric acid may not be dissociated in the solution. The other 10% of the citrates may stay in the solution in the form of H₃Cit Na⁺ that may, in turn, complex the In⁺⁺⁺ specie in the form of [(H₃Cit)In⁺⁺⁺]⁻⁻⁻⁻, where n may be in the range of 1-6 and m may be in the range of 0-3. As a result, most of In⁺⁺⁺ cations in the solution of the present invention are not complexed with the citrates. This is an important difference of the present invention from the literature (see, e.g. Fouda et al.). In Fouda a pH value of 5 was utilized. In the solution of the present invention In precipitates as In(OH)₃ at such pH values. Use of lower pH values allows the present solution to accommodate more In without precipitation and this improves plating efficiency and allows high current densities, which in turn reduces hydrogen evolution, improves the process throughput and therefore yields lower manufacturing cost. The solubility product of In(OH)₃ is 1×10⁻³³. The citrate seems to be a weak complexing agent for In. Therefore, the major role the citrates play in the solution of this embodiment of the present invention may not be complexing. Instead, there may be two aspects operating in our bath. On one hand, the sodium citrate may form a kind of buffer solution with the citric acid to stabilize the solution pH value. On the other hand, citrate may consume some excess protons to reduce hydrogen generation during the In plating process.

As mentioned before, a pH value of 5 was utilized in the work described by Fouda et al. Use of low pH values in the present invention provides several benefits including: i) adjustment of pH to low values can be achieved using citric acid instead of other acids. Citric acid is the acid of the citrate anions, which provide preferable plating results as explained before. ii) Using citric acid allows control of the cation concentration in the bath. If, for example, Na-citrate was used solely as a source of citrate, the Na concentration and citrate concentration in the bath would be tied together. By using citric acid in addition to its conjugated salt such as Na-citrate, we have independent means of controlling pH as well as the citrate concentration and Na concentration in the plating bath. This flexibility allows adjustment of the bath so that plating efficiencies close to 100% can be achieved for the first time.

The invention will now be further described with reference to certain examples, however the invention is not limited to the examples set forth herein. The electroplating experiments in these examples were carried out using a potentiostat/galvanostat (EG&G Model 263 A). The solutions were stirred during plating. De-oxygenation was not found to be necessary during the In plating process although this may be helpful in reducing the In anode oxidation during plating. The substrates for the plating tests included stainless steel and soda-lime glass, both coated with a contact layer comprising a Cu film on its surface. Indium was electroplated on the Cu surface and the results were evaluated. The surface areas for the substrates were varied from several cm² to several hundreds of cm² to understand the suitability of the method for large scale manufacture. After the In deposition, the uniformity and the plating efficiency were evaluated by dissolving various portions of the films and using Inductively Coupled Plasma (ICP) method to measure the In amounts in the dissolved samples.

EXAMPLE 1

In Plating Bath Containing Citrates

A set of exemplary aqueous plating solutions were prepared containing 0.1-0.3 M InCl₃, 0.2-0.5 M sodium citrate (Na₂C₆H₅O₇), and 0.1-0.3 M citric acid (H₃C₆H₅O₇). The pH was adjusted to a range between 1.5 and 3.5. Indium was electrodeposited on the Cu surfaces at current densities of 5-30 mA/cm². Highly adherent In films with surface roughness less than 10 nm were obtained for a thickness of 200-400 nm. The plating efficiency was measured and found to be in the 95-100% range. The typical anode used in the plating was an In plate. The result In films were shiny, silvery white, smooth and substantially defect free, as examined with SEM and optical microscopes. No hydrogen evolution could be observed during plating. Indium was also plated on other metal surfaces using the citrate In plating baths with high plating efficiency. An accelerated test that continuously lasted 80 hours demonstrated that the bath chemistry was stable without any oxide or hydroxide precipitation and the deposition efficiencies were repeatable. Another plating bath containing 50 liters of the In plating solution was used to plate In onto the 6”x8” substrates for nine months with repeatable results if the pH was adjusted about once in two weeks. The In⁺⁺⁺ concentration was stable if the In plate was used for the anode and did not require any adjustment. The In thickness was very repeatable and the non-uniformity over the whole 6”x8” substrates could be controlled at levels below 2% of relative standard deviation for different locations on the substrate.

The indium citrate solution containing 0.2 M InCl₃, 0.15 M citric acid, and 0.35 M sodium citrate (pH=2.0) was applied to a roll-to-roll plating line. The web substrate used in this roll-to-roll plating line was 13” wide and moved at a speed of about 2 ft/min. The current density used in the plating was about 10 mA/cm². This plating process produced uniform, smooth and defect free In films demonstrating the suitability of the solution to large scale manufacturing.

EXAMPLE 2

In Plating Bath Containing Glycine as the Complexing Agent

An aqueous plating bath was formulated with 0.2 M InCl₃, and 0.5 M Glycine to compare the bath of the present invention with a bath comprising a complexing agent. The pH was adjusted to the range of 2.0-2.5 using HCl. The plating
tests were carried out on Cu surfaces at current densities of 10-30 mA/cm². All the In films looked shiny and smooth but the cathodic plating efficiencies were only about 60-85%. Extensive hydrogen bubbling was observed on the cathode surface during the plating, which resulted in defects and pinholes on the In films that were visible to naked eye.

[0031] Example 1 above demonstrated the good performance of citric acid and its conjugate pair citrate in the In plating bath. It should be appreciated that other acids and their conjugate pairs may play the same roles in other In plating baths with a pH less than about 4.0, preferably less than about 3.5. These acids include but are not limited to acetic acid, tartaric acid, phosphoric acid, oxalic acid, carboxylic acid, ascorbic acid, boric acid, butanoic acid, thioacetic acid, glycolic acid, malic acid, formic acid, heptanoic acid, hexanoic acid, hydrocyanic acid, hydrofluoric acid, lactic acid, nitrous acid, octanoic acid, pentanoic acid, uric acid, sulfuric acid, sulfuric acid HSO₄⁻, nonanoic acid, decanoic acid, dodecanic acid, tetradecanoic acid, hexadecanoic acid, octadecanoic acid, eicosanoic acid, tetracosanoic acid, etc. All of these acids may be combined with Li⁺, Na⁺, K⁺, NH₄⁺ or (C₅H₁₁COO)⁻, e.g., where n may be 1 to 6) salts of their conjugate pairs and In⁺⁺ salts to form In plating baths with high efficiency.

[0032] Although water is the preferred solvents in the formulation of the In plating baths of the present invention, it should be appreciated that organic solvents may also be added in the formulation, partially or wholly replacing the water. Such organic solvents include but are not limited to alcohol, acetone, toluene, propylene carbonate, formamide, dimethyl sulfoxide, and glycerin.

[0033] Although the DC voltage/current was utilized during the In electroplating processes of the present invention, it should be noted that pulsed or other variable voltage/current sources may also be used to obtain high plating efficiencies and high quality In deposits employing the In plating baths of the present invention. The temperature of the In electroplating baths may be in the range of 5-120°C depending upon the nature of the solvent. It is preferable to keep this temperature below the boiling point of the solvent. The preferred bath temperature for water-based formulation is in the range of 10-60°C. The most preferred range is 15-30°C.

[0034] Although not preferable, the electroplating baths of the present invention may comprise additional ingredients. These include, but are not limited to, grain refiners, surfactants, dopants, other metallic or non-metallic elements, etc. For example, organic additives such as surfactants, suppressors, levelers, accelerators, etc. may be included in the formulation to refine its grain structure and surface roughness. Organic additives include but are not limited to polyvinylidene glycol type polymers, propane sulfonic acids, coumarin, saccharin, furfurral, acrylonitrile, magenta dye, glue, SPS, starch, dextrine, etc. In fact, dextrine and triethyleneamine were used in the In citrate baths of the present invention, but the difference is insignificant because the plated In films have already shown good qualities without any additives.

[0035] It should be noted that the present invention is directed to the electroplating of substantially pure In layers (more than about 99.5% In, preferably more than 99.9% In) since the electronics application and specifically CIGS(S) solar cell application of such layers require good thickness and compositional control. However, trace amounts of other materials may be included in the bath formulation of the present invention without changing its fundamentals. For example, small amounts (typically less than 0.01 M) Ga, Cu, S and/or Se may be present in the formulation, provided that they do not interfere with the high plating efficiency. The In layers produced using the bath compositions of the present invention were successfully employed to fabricate some all-electroplated metallic stacks on bases comprising stainless steel substrates coated with contact layers comprising Mo and/or Ru. These stacks had various deposition sequences yielding base/Cu/Ga/In/Se, base/Cu/Ga/Cu/In/Se, base/Cu/In/Cu/Ga/Se, base/Cu/Ga/Cu/In/Se and base/Ga/Cu/In/Se multiple layers. A Ga citrate based electroplating bath developed by the present inventors (US Pat Appl Pub. 20070272558) was utilized for Ga depositions. The stacks were then reacted in a tube furnace at 500°C for 50 minutes under inlet gas to form Cu(In,Ga)₅Se₅ absorbers. The Cu/(In+Ga) molar ratio was kept in the range of 0.8-0.9 while the Ga/(In+Ga) molar ratio was nominally 50% in these samples. After the reaction step, a 100 nm thick CdS layer was chemically deposited onto the absorber surfaces yielding a base/Cu(In, Ga)₅Se₅/CdS structure. A ZnO containing transparent oxide layer was then deposited over the CdS films by the sputtering technique. Solar cell was completed by printing Ni or Ag finger contacts over the transparent oxide layer. Solar cell efficiencies over 15% were recorded from these devices demonstrating the quality of the electrodeposited stacks comprising the In layers of the present invention. This efficiency value is the highest that has been achieved by a two stage process employing In electrodeposition for the precursor preparation.

What we claim is:

1. An electroplating solution for application of a substantially pure indium (In) film onto a conductive surface at high plating efficiency, comprising:
   a solvent;
   an In source providing In ions to the solvent with an In ion concentration of at least about 0.05 M; and
   a weak acid and a conjugate pair salt of the weak acid, wherein the pH value of the electroplating solution is below about 4.0,
   and wherein the weak acid is selected from the group consisting of citric acid, acetic acid, formic acid, thioacetic acid, glycolic acid, lactic acid, ascorbic acid, malic acid, butanoic acid, and pentanoic acid.

2. The solution of claim 1 wherein the weak acid is citric acid and the pH value is below 3.5.

3. The solution of claim 2, wherein the In source comprises at least one of In-chloride, In-sulfate, In-acetate, In-carbonate, In-nitrate, In-perchlorate, In-phosphate, In-oxide and In-hydroxide.

4. The solution of claim 3, wherein the conjugate salt is at least one of sodium citrate, lithium citrate, potassium citrate, and an organically modified citrate, wherein the organically modified citrate comprises a citrate moiety such that one or more organic groups replaces (a) one or more hydrogens that are directly connected to a carbon or oxygen bonded to carbon 2 of the citrate moiety, or (b) the hydroxy group bonded to carbon 2 of the citrate moiety.

5. The solution of claim 2, wherein the concentration of the In ions is at least 0.1M.

6. The solution of claim 5, wherein the pH value is below 2.5.

7. The solution of claim 5, wherein the solvent comprises water.
8. The solution of claim 2 such that it comprises no organic additives.

9. The solution of claim 1, wherein the solvent comprises water.

10. The solution of claim 1, wherein the In source comprises at least one of In-chloride, In-sulfate, In-acetate, In-carbonate, In-nitrate, In-perchlorate, In-phosphate, In-oxide and In-hydroxide.

11. A method of obtaining a substantially pure and substantially defect-free In film on a surface of a conductor comprising the steps of:

   providing a solution with a pH value below 4 that includes a solvent, an In source providing In ions to the solvent with an In ion concentration of at least 0.05 M, citric acid and a conjugate pair salt of citric acid;

   applying the solution onto an anode and the surface of the conductor, establishing a potential difference between the anode and the conductor, and

   electrodepositing the substantially pure In film on the surface of the conductor.

12. The method of claim 11 wherein the surface of the conductor comprises copper.

13. The method of claim 11 wherein the surface of the conductor comprises gallium.

14. The method of claim 11 further comprising the step of controlling the temperature of the solution within the range of 10-60°C. before the step of electrodeposition and wherein the In source comprises at least one of In-chloride, In-sulfate, In-acetate, In-carbonate, In-nitrate, In-perchlorate, In-phosphate, In-oxide and In-hydroxide.

15. The method of claim 14 wherein the In source comprises at least one of In-chloride, In-sulfate, In-acetate, In-carbonate, In-nitrate, In-perchlorate, In-phosphate, In-oxide and In-hydroxide.

16. The method of claim 15 wherein the conjugate pair salt of citric acid is at least one of sodium citrate, lithium citrate, potassium citrate, and an organically modified citrate.

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