



US 20130327651A1

(19) **United States**(12) **Patent Application Publication**
O'SULLIVAN et al.(10) **Pub. No.: US 2013/0327651 A1**(43) **Pub. Date: Dec. 12, 2013**(54) **PLATING BATHS AND METHODS FOR
ELECTROPLATING SELENIUM AND
SELENIUM ALLOYS**(75) Inventors: **EUGENE O'SULLIVAN**, NYACK, NY
(US); **LUBOMYR T. ROMANKIW**,
BRIANCLIFF MANOR, NY (US);
NAIGANG WANG, OSSINING, NY
(US)(73) Assignee: **INTERNATIONAL BUSINESS
MACHINES CORPORATION**,
ARMONK, NY (US)(21) Appl. No.: **13/523,179**(22) Filed: **Jun. 14, 2012****Related U.S. Application Data**(63) Continuation of application No. 13/490,488, filed on
Jun. 7, 2012.**Publication Classification**(51) **Int. Cl.**
C25D 3/02 (2006.01)
C25D 3/56 (2006.01)
(52) **U.S. Cl.**
USPC **205/239**; 205/316(57) **ABSTRACT**

Plating bath solutions and methods for depositing selenium generally include an aqueous plating bath containing a soluble selenium source and a soluble surfactant additive, wherein the soluble surfactant additive is selected from the group consisting of an alkane sulfonic acid, an alkane phosphonic acid and mixtures thereof, wherein the alkane group defining the alkane sulfonic acid and the alkane phosphonic acid has less than 25 carbon atoms. The method includes immersing a conductive substrate to be plated into the aqueous plating bath; and electroplating selenium onto the substrate to form a continuous and particle free film.

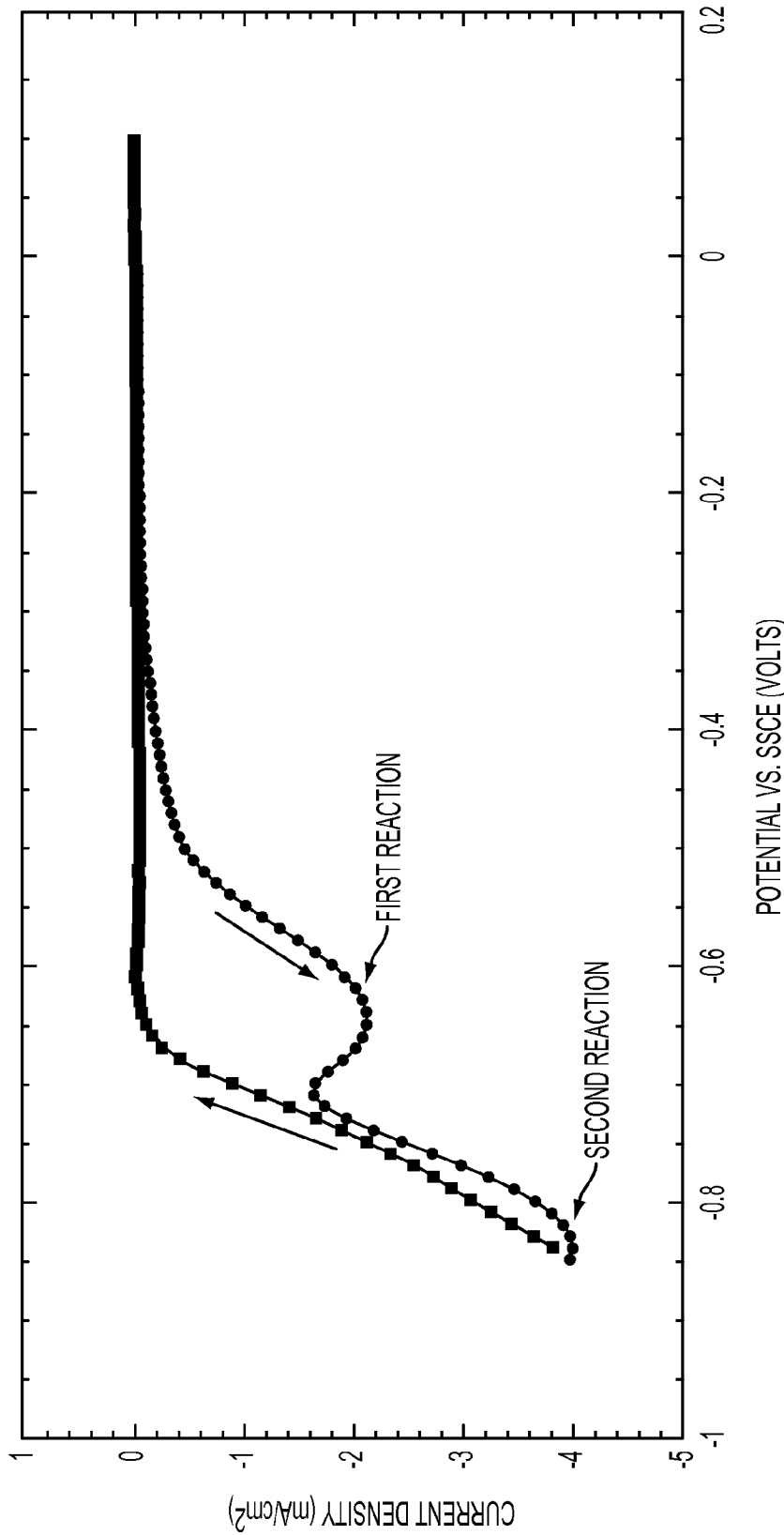


FIG. 1

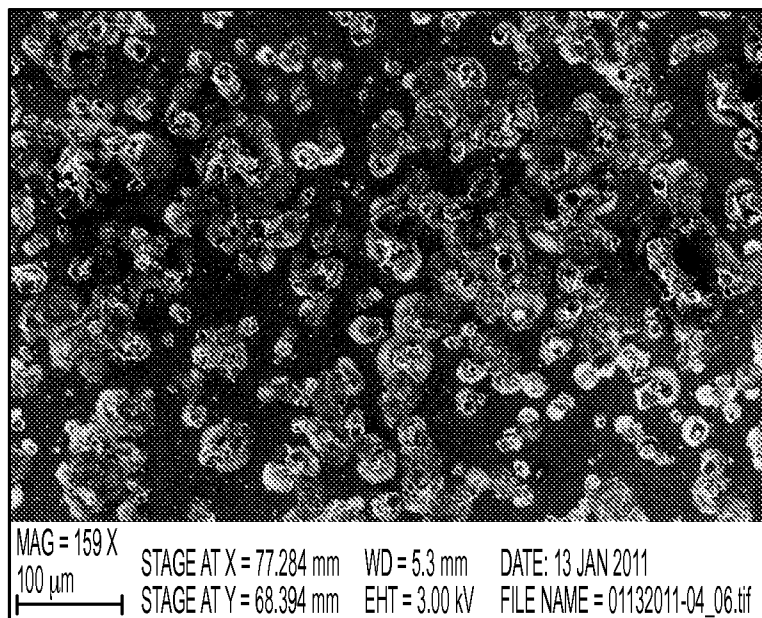


FIG. 2A

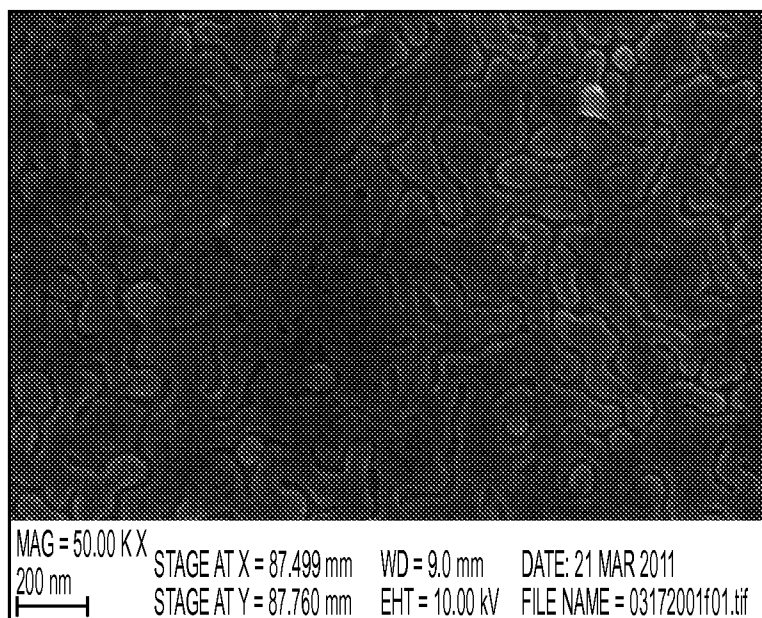


FIG. 2B

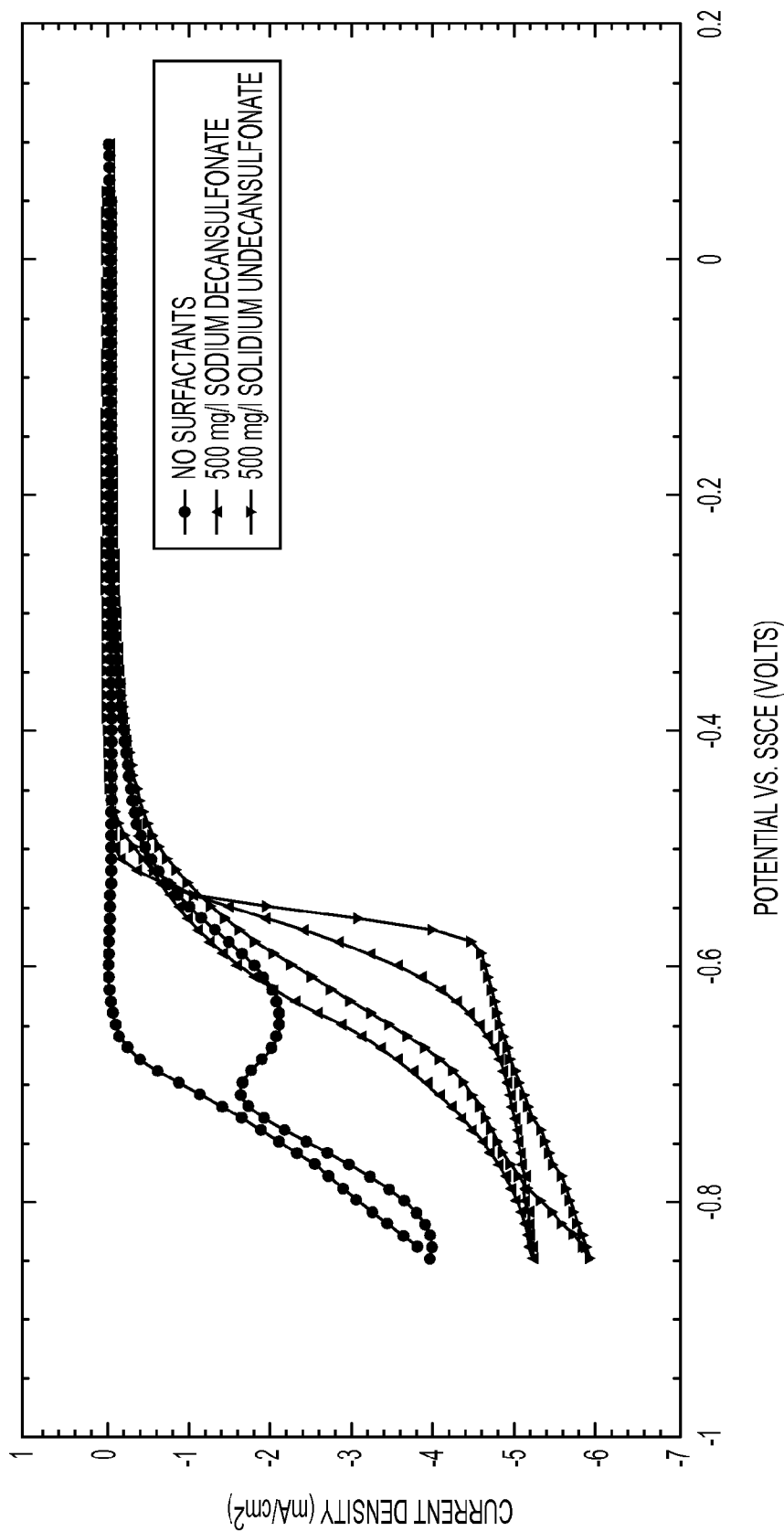


FIG. 3

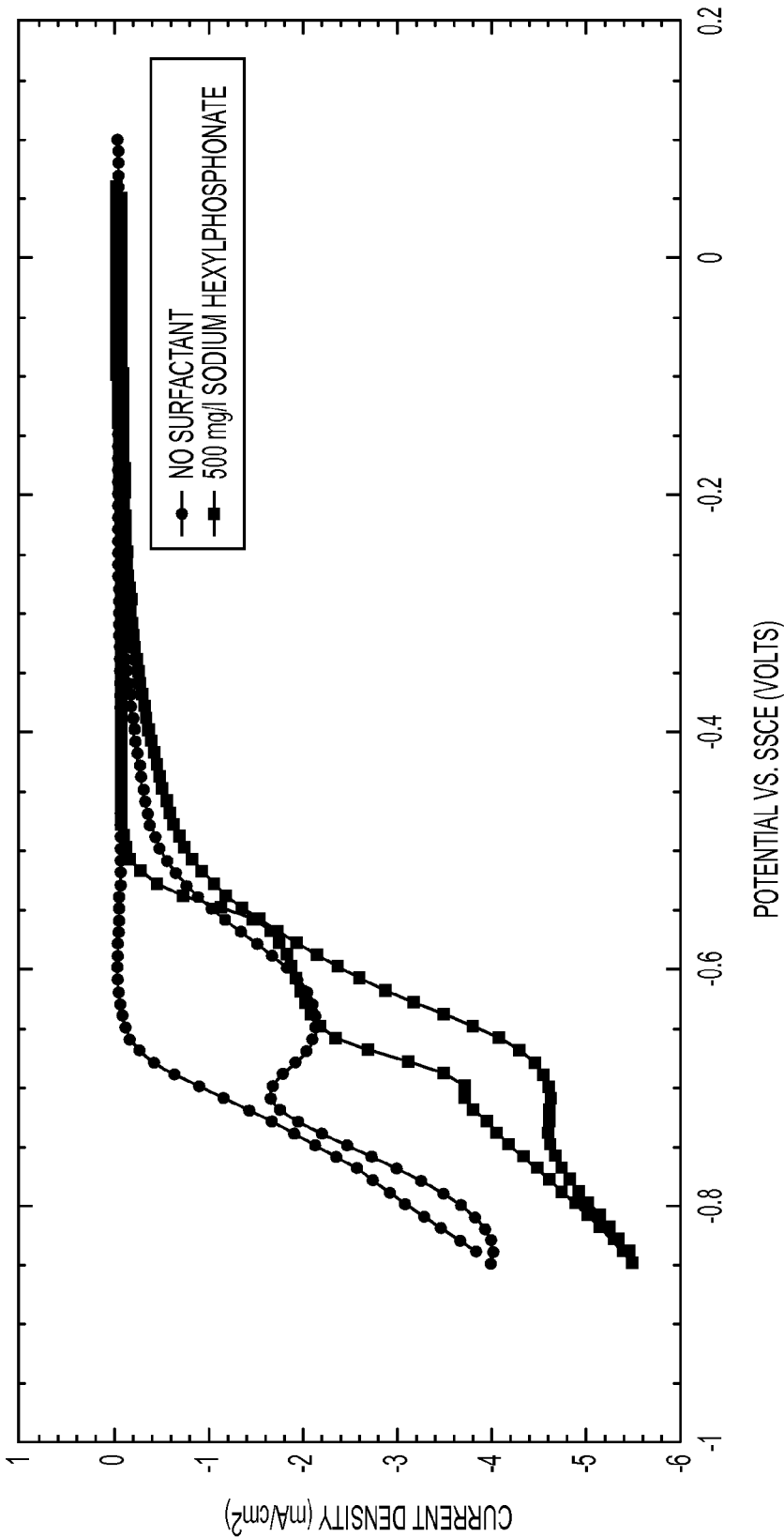


FIG. 4

PLATING BATHS AND METHODS FOR ELECTROPLATING SELENIUM AND SELENIUM ALLOYS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation application of and claims priority to U.S. application Ser. No. 13/490,488, filed on Jun. 7, 2012, incorporated herein by reference in its entirety.

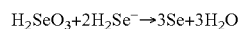
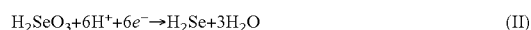
BACKGROUND

[0002] The present disclosure generally relates to electroplating, and more particularly to, electroplating selenium and selenium alloys in an aqueous solution.

[0003] Electroplating is a plating process in which metal ions in a solution are moved by an electric field to a substrate, e.g., an electrode, to form a film thereon. Electroplating is primarily used for depositing a layer of material to bestow a desired property (e.g., wear resistance, lubricity, aesthetic qualities, etc.) to a surface that otherwise lacks that property. The part to be plated is typically the cathode and the other part is the anode of the circuit. Both components are immersed in an electrolyte and a power supply supplies a direct current to the anode. At the cathode, the metal ions in the electrolyte solution are reduced at the interface between the solution and the cathode, such that they “plate out” onto the cathode to form a film.

[0004] Selenium is a semiconductor material that is widely used in electronic industries, such as in the manufacture of photovoltaic devices and optoelectronic devices. Additionally, selenium can be used as spacer layers for on-chip inductors/transformers and thin film recording heads, which usually contain a magnetic core/yoke. Due to its relatively high resistivity, selenium can be used to laminate magnetic core materials to control magnetic domains and decrease eddy current losses. For this purpose, the selenium layer is relatively thin, e.g., about 10 to about 500 nanometers, uniform, free of pin-holes, and free of defects, e.g., particles.

[0005] Selenium electroplating generally involves the following two electrochemical reaction schemes depending on the applied potential.



[0006] Controlling the plating process to obtain continuous, particle-free films has proven to be difficult. The current density induced from the first reaction (I) is much lower than that of the second reaction (II). However, in practice, a higher current density is often desired in order to maintain a high deposition rate. At high current density, however, the second reaction dominates, which brings a common problem of plating selenium and selenium alloys. As indicated in the above reaction schemes, the second reaction (II) produces an intermediate phase H_2Se , which is a gas. H_2Se will further react rapidly with the H_2SeO_4 ions in the solution to form Se colloids at the surface of the cathode. Many of the colloids will become trapped inside of the films, which can lead to coating defects in the form of particle inclusions as well as result in powdery films depending on the amount of particles formed.

[0007] The presence of the selenium particles within the deposited film can disturb the uniformity of the electroplated selenium layer, cause surface roughness and affect the kinetics of reaction between the selenium layer and an underlying precursor film such as may occur in the manufacture of a photovoltaic cell when the stack is heated to form a compound absorber layer. For example, if the precursor film is a copper-indium layer and if the stack is heated up to over 400°C . to react the copper, indium, and deposited selenium species to form a CIS compound film on the surface of the substrate, the reaction kinetics would be very different due to the presence of a large selenium particle, which would change the molar ratio between the species when heated. Such compositional differences between portions of the stack create morphological, electrical, and compositional differences between corresponding portions of the compound CIS layer obtained after the reaction step, reduce its uniformity, and thus reduce the efficiencies of the photovoltaic cells that may be fabricated on such non-uniform layers. It should be noted that the thickness of electroplated selenium layers may be in the range of 50-5000 nm whereas the size of the selenium particles may range between 500-10000 nm, depending upon the length of the electrodeposition period.

[0008] As previously noted, the selenium particles typically form near the cathode surface. Some of these particles may get trapped into the growing selenium film on the cathode and others may precipitate onto other wetted surfaces of the electrodeposition system, thereby becoming a source of particles and defectivity throughout the electrodeposition process. This is very undesirable, especially for continuous manufacturing processes such as roll-to-roll electroplating, since deposition in such systems continues uninterrupted for several hours and even for several days. Stopping the electrodeposition process for cleaning the wetted parts to eliminate selenium particles is time consuming, expensive, and impractical. Furthermore, formation of selenium particles, which may stay close to the surface of the cathode and grow in size depletes the dissolved selenium concentration in the plating bath fast. As a result, the concentration of selenium in the solution decreases with time, leading to bath stability problems. The formation of colloidal amorphous selenium particles is not only observed in electrodeposition of pure selenium layers but also occurs during electroplating of metal selenides such as In—Se, Ga—Se, Cu—Se, Cu—In—Se, Cu—Ga—S, and the like. The generation of colloidal particles might also be present in plating applications where other group VIB elements such as tellurium and sulfur are electrodeposited either in the form of pure elemental layers or co-deposited with Se such as sulfur-selenium 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.

[0009] In the past, several methods have been attempted to control particle formation. For example, U.S. Pat. No. 2,649, 409 to Von Hippel et al. discloses electroplating at high temperatures so that the colloids and/or particles purportedly can be dissolved during the deposition process. There, the patents disclosed that gray crystalline metallic selenium may be electroplated using an acidic electrolyte composed of saturated selenium oxide in 9 molar H_2SO_4 at a temperature of 100°C . However, the high temperatures employed in this process limit its commercial manufacturability.

[0010] Other methods such as those described in US Patent Publication No. 2009/0283411 to Aksu et al. include the use

of anti-coagulation agents to inhibit selenium particle growth and promote selenium particle dispersal. However, even with the anticoagulation agent, some particles can still be present in the films. Moreover, the process requires particles in the solution to be continually filtered.

[0011] If plating is performed at less negative potential with very low current density to trigger only the first reaction, not only is the deposition rate low but the resulting films tend to be discontinuous due to the low deposition nucleation that occurs. Although the discontinuous microstructure often occurs at an early stage of deposition, it can affect the microstructure and roughness of the resulting films. These discontinuous microstructures are much easier formed on common seed layers for selenium deposition such as copper, nickel, cobalt and iron based magnetic materials. Because Se is a noble metal, selenium ions will replace these metal atoms in the seed layer through a displacement reaction, which will often result in discontinuous films. For this reason, previous reports often use seed layers such as indium tin oxide or titanium to prevent the displacement reactions from occurring, which as noted above limits the application of selenium materials.

SUMMARY

[0012] Disclosed herein are plating solutions and methods for electroplating selenium onto a substrate. In one embodiment, an electroplating solution for plating selenium on a substrate comprises at least one bath soluble selenium source; at least one bath soluble surfactant additive of the formulae RSO_3H and/or RH_2PO_3 , wherein R is an alkyl group of 1 to 25 carbon atoms; and a solvent, wherein the solution is at a pH of about 2 to about 4 and is at a temperature of about 15° C. to about 45° C.

[0013] In another embodiment, an electroplating solution for plating selenium alloys on a substrate comprises at least one bath soluble selenium sources selected from the group consisting of selenium oxide, selenious acid, and mixtures thereof; at least one of indium ions, gallium ions and copper ions; at least one bath soluble surfactant additive of the formulae RSO_3H and/or RH_2PO_3 , wherein R is an alkyl group of 1 to 25 carbon atoms; and a solvent, wherein the solution has a pH within a range of about 2 to about 4 and is at a temperature within a range of about 18° C. to about 25° C.

[0014] The disclosure may be understood more readily by reference to the following detailed description of the various features of the disclosure and the examples included therein.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0015] Referring now to the figures wherein the like elements are numbered alike:

[0016] FIG. 1 graphically illustrates a cyclic voltammetry trace for a 0.1 M selenium electroplating solution without an additive.

[0017] FIGS. 2A and 2B depicts scanning electron micrographs of selenium film electroplated without an additive at a current density of 5 mA/cm² and 0.5 mA/cm², respectively.

[0018] FIG. 3 graphically illustrates a cyclic voltammetry traces for a selenium electroplating solution without an additive, and selenium plating solutions in accordance with the present disclosure including decanesulfonic acid or undecanesulfonic acid as the surfactant additive.

[0019] FIG. 4 graphically illustrates a cyclic voltammetry traces for a selenium electroplating solution without an additive, and a selenium plating solution in accordance with the present disclosure including sodium hexylphosphonate as the surfactant additive.

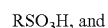
DETAILED DESCRIPTION

[0020] Disclosed herein are methods and plating bath solutions for electroplating selenium. The plating bath solutions contain surfactant additives that markedly enhance the low-potential selenium deposition and avoid forming selenium particles at high potential while maintaining a high deposition rate. As will be described in greater detail herein, the presence of the surfactant additives in the plating bath promotes formation of a continuous selenium coating via the above reaction scheme (I) and further enhances the first reaction so that a high deposition rate can still be maintained. Advantageously, the plating method produces continuous and particle-free selenium and selenium-alloy films.

[0021] The selenium electroplating bath solution of the present disclosure may be prepared by; i) dissolving a desired amount of at least one selenium (Se) ion source, such as selenous acid (i.e., H_2SeO_3 ; also referred to as selenious acid) or selenium oxide (SeO_2) or mixtures thereof in a solvent such as water, ii) adding to the solution at least one soluble surfactant additive in accordance with the present disclosure, and iii) adjusting the pH of the solution by adding an acid. Exemplary non-limiting acids include sulfuric acid, nitric acid, hydrochloric acid, and the like. The presence of the at least one surfactant additive has been found to promote formation of a continuous selenium coating via the above reaction scheme (I) and further enhance the first reaction so that a high deposition rate can still be maintained.

[0022] The total concentration of the selenium ions in the bath may vary over a wide range depending on the desired properties. Generally, selenium metal ions are present in the plating bath in an amount from about 0.001 to about 1 molar (M). In other embodiments, the selenium metal ion present in the bath is about 0.01 to about 1 M, and in still other embodiments, the selenium metal ion present in the bath is about 0.1 to about 1 M.

[0023] The surfactant additive is preferably a lower alkane sulfonic acid or lower alkane phosphonic acid or salt thereof of the general formulae:



wherein R is an alkyl group containing from about 1 to about 25 carbon atoms. In other embodiments, R is an alkyl group containing from about 1 to 18 carbon atoms, and in still other embodiments, R is an alkyl group containing 1 to 12 carbon atoms. The alkyl group may be branched or linear. Suitable surfactant additives of the general formula above are soluble in the selected solvent, e.g., water. Non-limiting alkane sulfonic acid surfactant additives includes, without limitation, propane sulfonic acid, 2-propane sulfonic acid, decanesulfonic acid, undecanesulfonic acid, and the like. Non-limiting alkane phosphonic acid surfactant additives includes, without limitation, propylphosphonic acid, butylphosphonic acid, hexylphosphonic acid, octylphosphonic acid, dodecylphosphonic acid, and the like. The surfactant additive is soluble in the selected solvent, e.g., water.

[0024] The concentration of the surfactant additive in the plating baths is about 1 milligram to 1 gram per liter. In other embodiments, the concentration of the surfactant additive in the plating baths is about 5 to 750 milligrams per liter, and in still other embodiments, the concentration of the surfactant additive in the plating baths is about 10 to 250 milligrams per liter.

[0025] Although water is the preferred solvent in the formulation of the plating baths, 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 alcohols, acetonitrile, propylene carbonate, formamide, dimethyl sulfoxide, glycerin etc.

[0026] Optionally, the electroplating bath may further include other additives typically employed in electroplating baths including, but not limited to, organic acids, brighteners, buffers, chelating species, and the like. Exemplary brighteners are well known and generally include sulfonamides, sulfonimides, benzene sulfonic acids, naphthalenesulfonic acids, and the like. Exemplary chelating species include ethylenediamine tetraacetic acid (EDTA), ethylenediaminetetra-2-hydroxypropoane (quadrol), malic acid, citric acid, mannitol, sorbitol, and the like.

[0027] The pH of the selenium electroplating solution in accordance with the present disclosure may be adjusted to the range of about 2 to about 4. In still other embodiments, the pH is adjusted to about 3 to about 4.

[0028] The electroplating bath operating temperature can generally range from about 15° C. to about 45° C. In some embodiments, the electroplating bath operating temperature is at about 18 to about 25° C. In still other embodiments, the electroplating bath operating temperature is at about room temperature, e.g., about 20 to about 22° C.

[0029] Plating current densities are typically on the order of about 0.5 to about 20 mA/cm² and deposition times may vary from about 30 minutes to several hours or more. In other embodiments, the current densities are about 1 to about 10 mA/cm² and in still other embodiments, the current densities are about 1 to about 5 mA/cm². Although DC voltage/current can be utilized during the electrodeposition processes, it should be noted that pulsed or other variable voltage/current sources may also be used to obtain high plating efficiencies and high quality deposits. If a pulsed current is used, the current density will generally be higher, e.g., about double the current density in the steady state.

[0030] A number of sequential electroplating and annealing steps may be utilized to obtain the desired thickness of the selenium layer on a workpiece. The workpiece can be a semiconductor or any other substrate with a conductive surface. In one embodiment, the workpiece is a continuous flexible workpiece for roll-to-roll manufacture of solar cell absorbers. An exemplary continuous workpiece used in the process may have a length of 1 to 2000 meters with a width of 0.1 to 2 meters. The continuous flexible workpiece may include base having a conductive substrate and a contact layer such as a precursor layer including copper, gallium, and indium metals for example.

[0031] One notable advantage of the present techniques is that the electroplating process and Se electroplating solutions described herein can be used to form Se alloy films (e.g., CIS, CIGS, CZTS) that can serve, for example, as an absorber layer in photovoltaic devices. An exemplary photovoltaic device and method for the fabrication thereof will now be

described. It is to be understood however that there are many different possible photovoltaic device configurations.

[0032] In one embodiment, a p-type absorber layer is formed adjacent to the substrate. Namely, the substrate (with the metal layer) is placed directly into a plating bath solution prepared in accordance with the present disclosure. In this case, the electroplating solution contains a selenium source and one or more surfactant additives selected from the group consisting of alkane sulfonic acids, alkane phosphonic acid, salts thereof, and mixtures thereof. In addition to the selenium source and the surfactant additive, the electroplating solution may further contain one or more metal salts. The particular metal salt(s) used depends on the desired composition of the absorber layer. By way of example only, the electroplating solution would contain a Cu salt and an In salt if a CIS absorber layer is desired. The further addition of a Ga salt would result in a CIGS absorber layer. A Cu salt, a Zn salt and a Sn salt would be employed for a CZTS absorber layer. Suitable Cu, In, Ga, Zn and Sn salts were provided above. Electroplating is then used to form the absorber layer (e.g., CIS, CIGS, CZTS) on the substrate over the metal layer. The plating time can be tailored to the desired thickness of the resultant absorber layer, with a longer plating time being used to attain a thicker layer. According to an exemplary embodiment, the absorber layer is formed on the substrate to a thickness of from about 1 nm to about 1 micrometer (μm).

[0033] Alternatively, the selenium layer can be directly plated onto Cu, In or Ga containing surfaces to form precursor stacks having various configurations. Such configurations include, but are not limited to Cu/In/Se, Cu/In/Ga/Se, Cu—Ga/In/Se, and the like, and they may be used to manufacture CIS or CIGS type solar cell absorber films. One method of growing CIS or CIGS absorber films using electroplating is the “two-stage” process. In the two-stage process, controlled amounts of Cu, In, Ga and 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/Se, Ga/Cu/In/Se, In/Ga/Cu/Ga/Se, In/Ga/Cu/In/Se, Ga/In/Cu/Ga/Se, Ga/In/Cu/In/Se, Cu/Ga/Cu/In/Se, Cu/In/Cu/Ga/Se or the like. These stacks may then be annealed, or reacted, optionally with more Se, sulfur (S), tellurium (Te) 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 as well as Se layers within the precursor stacks, the process yield in terms of compositional control may be improved compared to the prior-art methods.

[0034] The present method, as compared to conventional evaporation or sputtering, will be cheapest, allow a high rate of deposition as well as improve the adhesion of the absorber layer to its back contact materials. Evaporation and/or sputtering, aside from the high cost, also have poor selectivity. Electrodeposition has 100% selectivity and is a low cost method of deposition utilizing solutions.

[0035] The following examples are presented for illustrative purposes only, and are not intended to limit the scope of the invention. In the following examples, the cyclic voltammetry studies were carried out using a three electrode cell consisting of an Ag/AgCl reference electrode (SSCE), a Pt rotational disc, and a Pt wire counter electrode. The scan direction of the cyclic voltammogram traces are indicated by arrows, where indicated.

Comparative Example 1

[0036] In this example, voltammetry curves of a selenium electroplating solution without an additive was examined, the results of which are shown in FIGS. 1 and 2. The selenium electroplating solution included a 0.1 Molar aqueous solution of selenium oxide (SeO_2) in sulfuric acid at a pH of 3 and at room temperature of about 21° C. The rotation speed was 200 rpm. Scan rate was 5 mV/s.

[0037] As shown in the voltammetry curve of FIG. 1, hydrogen evolution from a pH water curve (not shown) was observed at -0.42V. For the 0.1M Se^{4+} solution, although all of the reactions overlapped with hydrogen evolution, distinguished peaks are well defined. The peak at -0.6V is associated with Se reduction in accordance with reaction scheme (I) whereas the second peak at about 0-0.8V is caused by Se reduction in accordance with reaction scheme (II). For reasons previously discussed, because the H_2Se generated in the second reaction is in the gaseous phase, the solution will form particles and/or a colloid in the solution and at the seed layer interface.

[0038] FIG. 2A depicts scanning electron micrographs that clearly show evidence of a powdery film deposit when electroplating at a current density of 5 mA/cm². Lowering the current density to 0.5 mA/cm² resulted in a discontinuous film as shown in FIG. 2B.

Example 1

Surfactant Additive: Sodium Decanesulfonate or Sodium Undecanesulfonate

[0039] In this example, voltammetry curves of selenium electroplating solutions in accordance with the present disclosure including two different surfactant additives were examined using a rotating disk electrode, the results of which are shown in FIG. 3. In one example, the selenium electroplating solution included a 0.1 Molar aqueous solution of selenium oxide (SeO_2) and 500 milligrams/liter of sodium decanesulfonate at a pH of 3 and at room temperature. In the other example, the selenium electroplating solution included a 0.1 Molar aqueous solution of selenium oxide (SeO_2) and 500 milligrams/liter of sodium undecanesulfonate at a pH of 3 and at room temperature. The rotation speed in each experiment was 200 rpm.

[0040] As shown in FIG. 3, the addition of surfactant additives: sodium decanesulfonate or sodium undecanesulfonate substantially eliminated any indication of selenium reduction in accordance with reaction scheme (II). As shown, the barrier between the first and second selenium reduction almost disappeared completely. Moreover, the current of the first reaction (I) was about double compared to the selenium trace without any additive. Still further, the reverse curve is under the forward curve indicating facile nucleation and growth on selenium layers.

Example 2

Surfactant Additive: Sodium Hexylphosphonate

[0041] In this example, voltammetry curves of selenium electroplating solutions in accordance with the present disclosure including a surfactant additive were examined using a rotating disk electrode, the results of which are shown in FIG. 3. In this example, the selenium electroplating solution included a 0.1 Molar aqueous solution of selenium oxide

(SeO_2) and 500 milligrams/liter of sodium hexylphosphonate at a pH of 3 and at room temperature. The rotation speed in each experiment was 200 rpm.

[0042] As shown in FIG. 4, the addition of surfactant additives: sodium hexylphosphonate enhanced reaction scheme (I).

Example 3

[0043] In this example, selenium films were electroplated with selenium electroplating solution included a 0.1 Molar aqueous solution of selenium oxide (SeO_2) and 550 milligrams/liter of sodium 1-undecanesulfonate or 250 milligrams/liter of sodium hexylphosphonate/hexylphosphonic acid at a pH of 3 and at room temperature. Current density for the electroplated films was 2.5 mA/cm² without agitation. Scanning electron micrographs of the electroplated selenium films showed continuous particle free films.

[0044] All ranges disclosed herein are inclusive of the endpoints, and the endpoints are combinable with each other.

[0045] All cited patents, patent applications, and other references are incorporated herein by reference in their entirety.

[0046] The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting of the disclosure. As used herein, the singular forms “a”, “an” and “the” are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will be further understood that the terms “comprises” and/or “comprising,” when used in this specification, specify the presence of stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, elements, components, and/or groups thereof.

[0047] The corresponding structures, materials, acts, and equivalent of all means or step plus function elements in the claims below are intended to include any structure, material, or act for performing the function in combination with other claimed elements as specifically claimed. The description of the present disclosure has been presented for purposes of illustration and description, but is not intended to be exhaustive or limited to the disclosure in the form disclosed. Many modifications and variations will be apparent to those of ordinary skill in the art without departing from the scope and spirit of the disclosure. The embodiment was chosen and described in order to best explain the principles of the invention and the practical application, and to enable others of ordinary skill in the art to understand the disclosure for various embodiments with various modifications as are suited to the particular use contemplated.

What is claimed is:

1. An electroplating solution for plating selenium on a substrate comprises:

at least one bath soluble selenium source;

at least one bath soluble surfactant additive of the formulae RSO_3H and/or RH_2PO_3 , wherein R is an alkyl group of 1 to 25 carbon atoms; and

a solvent, wherein the solution is at a pH of about 2 to about 4 and is at a temperature of about 15° C. to about 45° C.

2. The electroplating solution of claim 1, wherein the at least one bath soluble selenium source is selected from the group consisting of selenium oxide and selenous acid.

3. The electroplating solution of claim 1, wherein the alkyl group is 1 to 12 carbon atoms.

4. The electroplating solution of claim 1, wherein the at least one bath soluble selenium source is in an amount of about 0.001 M to about 1 M.

5. The electroplating solution of claim 1, wherein the at least one bath soluble selenium source is in an amount of about 0.01M to about 1 M.

6. The electroplating solution of claim 1, wherein the at least one bath soluble surfactant additive is at a concentration of about 1 milligram per liter to 1 grams per liter.

7. The electroplating solution of claim 1, wherein the at least one bath soluble surfactant additive is at a concentration of about 5 milligram per liter to 750 milligrams per liter.

8. The electroplating solution of claim 1, wherein the at least one bath soluble surfactant additive is at a concentration of about 10 milligrams per liter to 250 milligrams per liter.

9. The electroplating solution of claim 1, wherein the bath is at a pH of about 3 to about 4 and is at a temperature of about 15° C. to about 45° C.

10. The electroplating solution of claim 1, further comprising at least one of indium ions, gallium ions and copper ions.

11. The electroplating solution of claim 1, wherein the bath is acidic.

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

13. An electroplating solution for plating selenium alloys on a substrate comprises:

at least one bath soluble selenium sources selected from the group consisting of selenium oxide, selenious acid, and mixtures thereof;

at least one of indium ions, gallium ions and copper ions; at least one bath soluble surfactant additive of the formulae RSO_3H and/or RH_2PO_3 , wherein R is an alkyl group of 1 to 25 carbon atoms; and

a solvent, wherein the solution has a pH within a range of about 2 to about 4 and is at a temperature within a range of about 18° C. to about 25° C.

14. The electroplating solution of claim 13, wherein the solvent comprises water.

15. The electroplating solution of claim 13, wherein the at least one bath soluble surfactant additive is at a concentration of about 10 milligram per liter to 100 milligrams per liter.

16. The electroplating solution of claim 13, wherein the surfactant additive is selected from the group consisting of decane sulfonic acid, undecanesulfonic acid, hexylphosphonic acid, salts thereof, and mixtures thereof.

17. The electroplating solution of claim 13, wherein the at least one bath soluble selenium source is in an amount of about 0.001 M to about 1 M.

18. The electroplating solution of claim 13, wherein the at least one bath soluble selenium source is in an amount of about 0.01 M to about 1 M.

* * * * *