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(54) **LIQUID PRECURSOR FOR DEPOSITION OF  
COPPER SELENIDE AND METHOD OF  
PREPARING THE SAME**

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(57) **ABSTRACT**

Liquid precursors containing copper and selenium suitable for deposition on a substrate to form thin films suitable for semiconductor applications are disclosed. Methods of preparing such liquid precursors and methods of depositing a precursor on a substrate are also disclosed.

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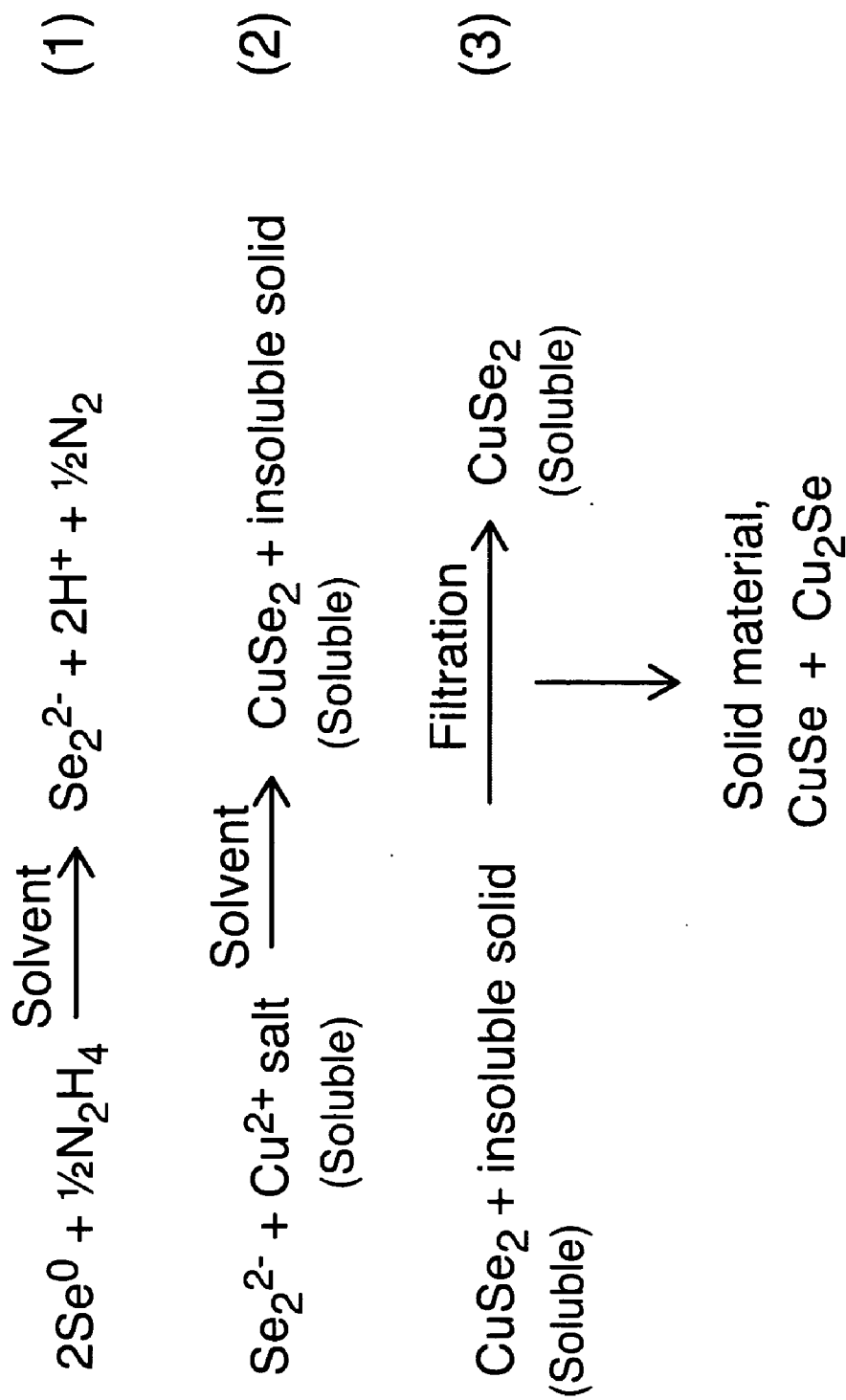


FIG. 1

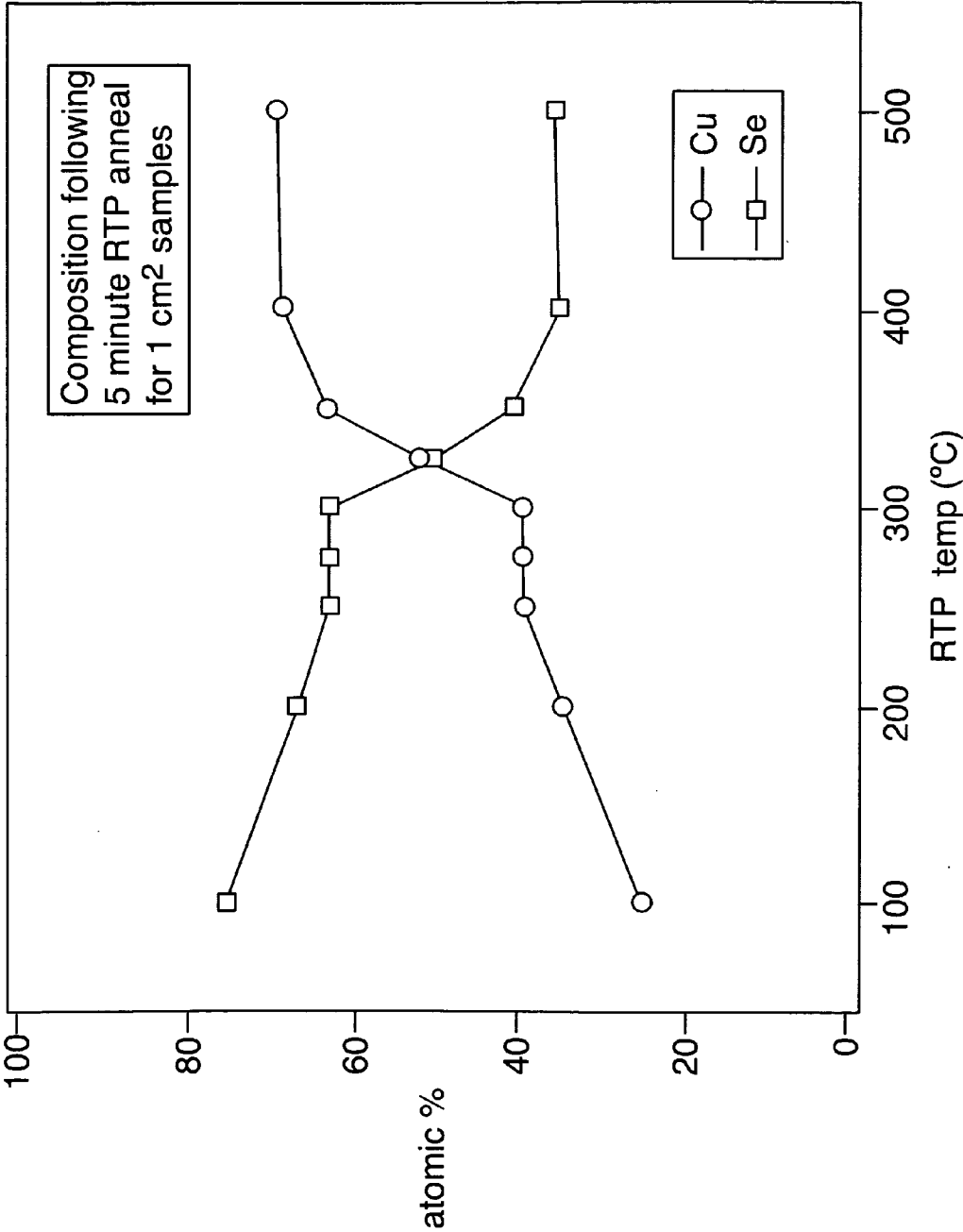
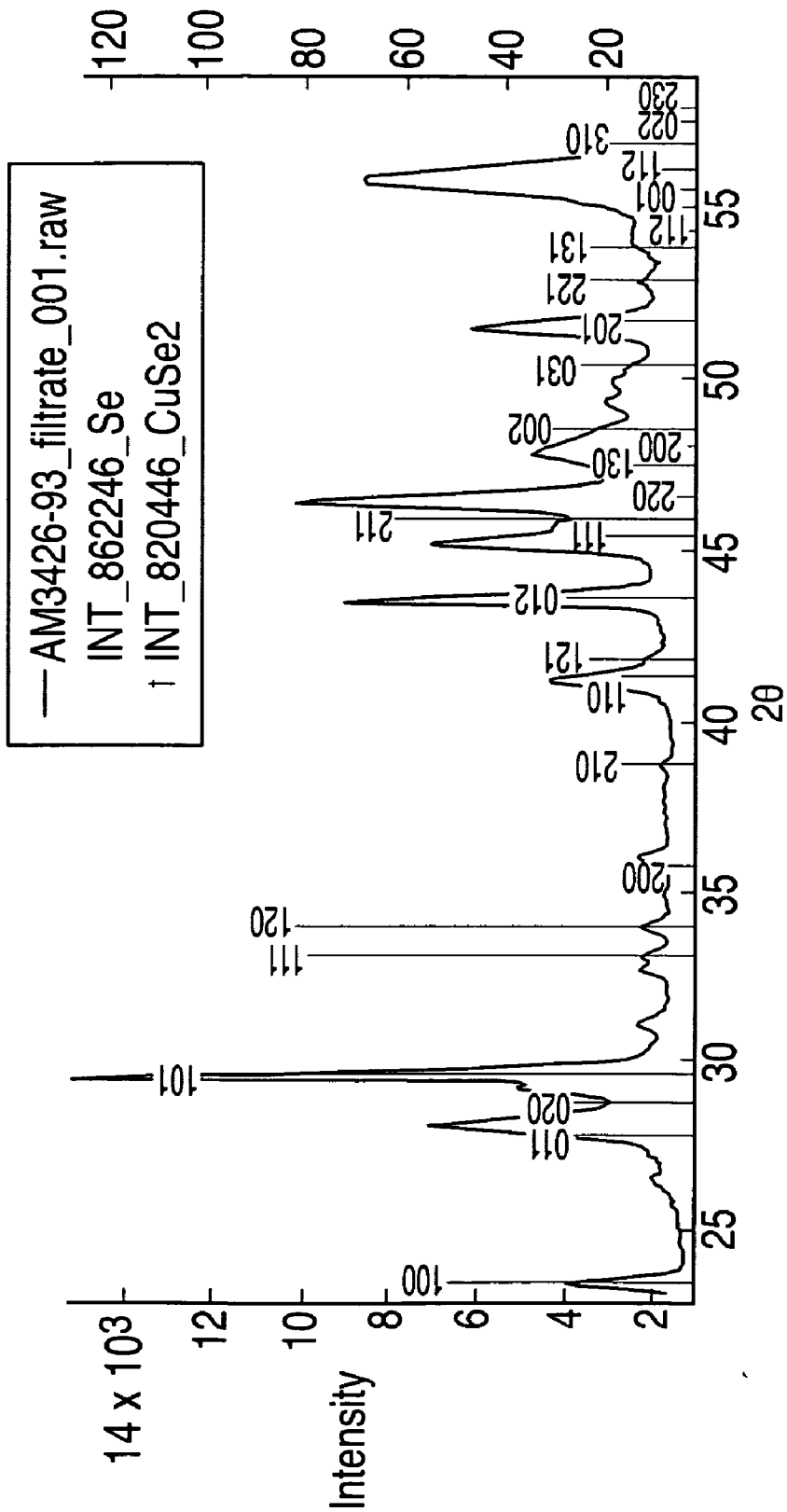
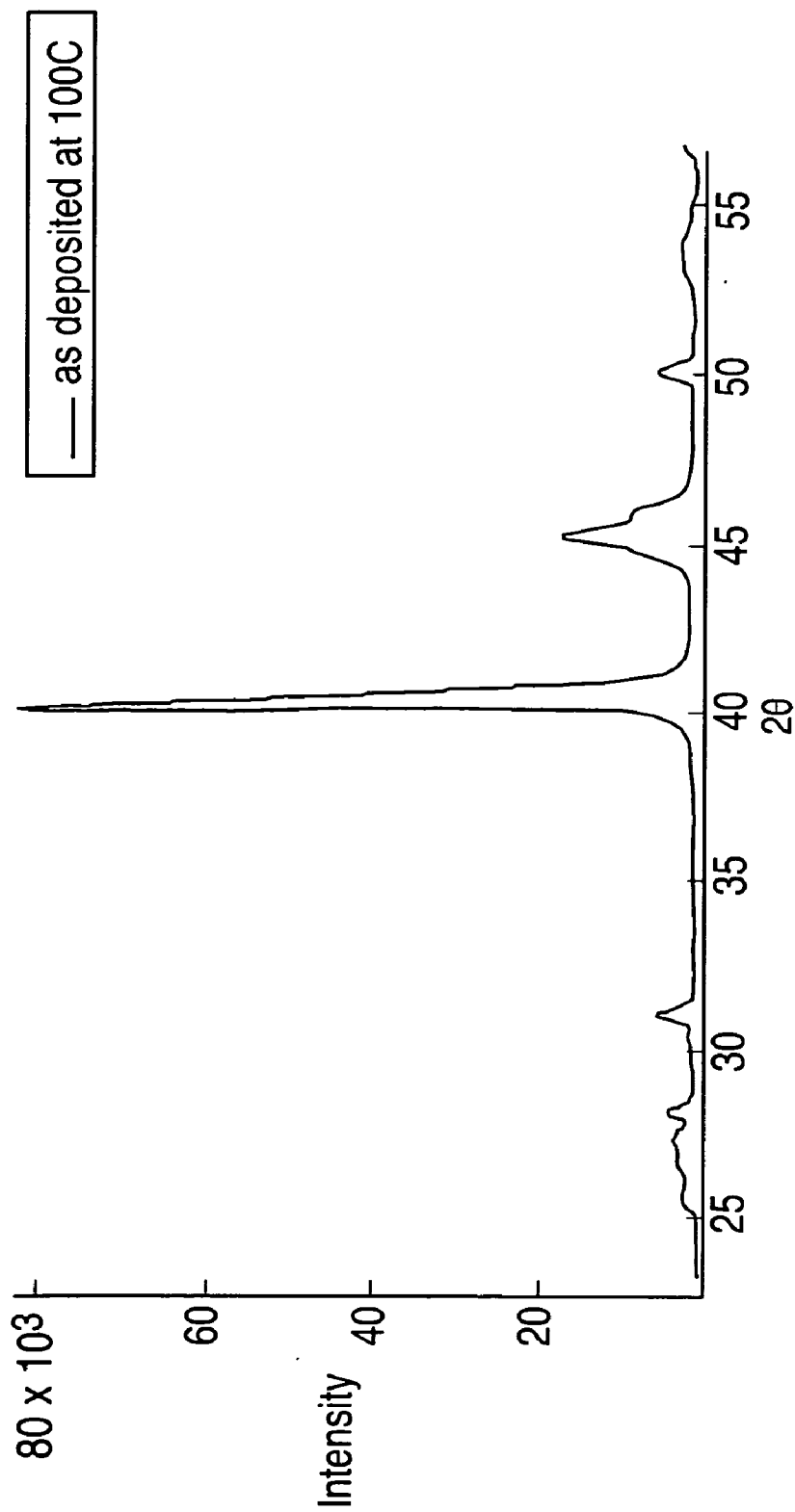


FIG. 2



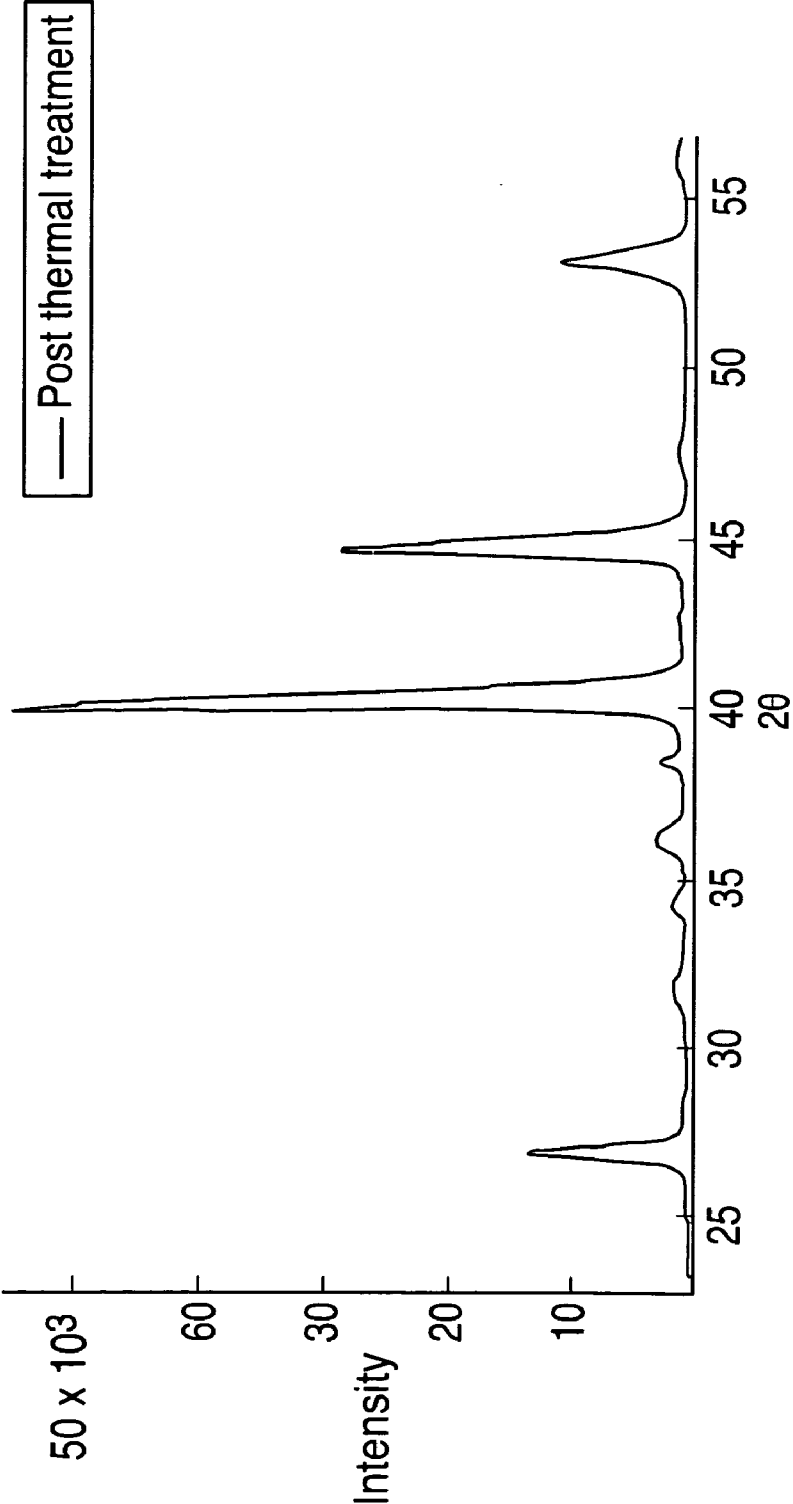
XRD Trace of Cu-Se film dropcast on glass at 200C.

FIG. 3



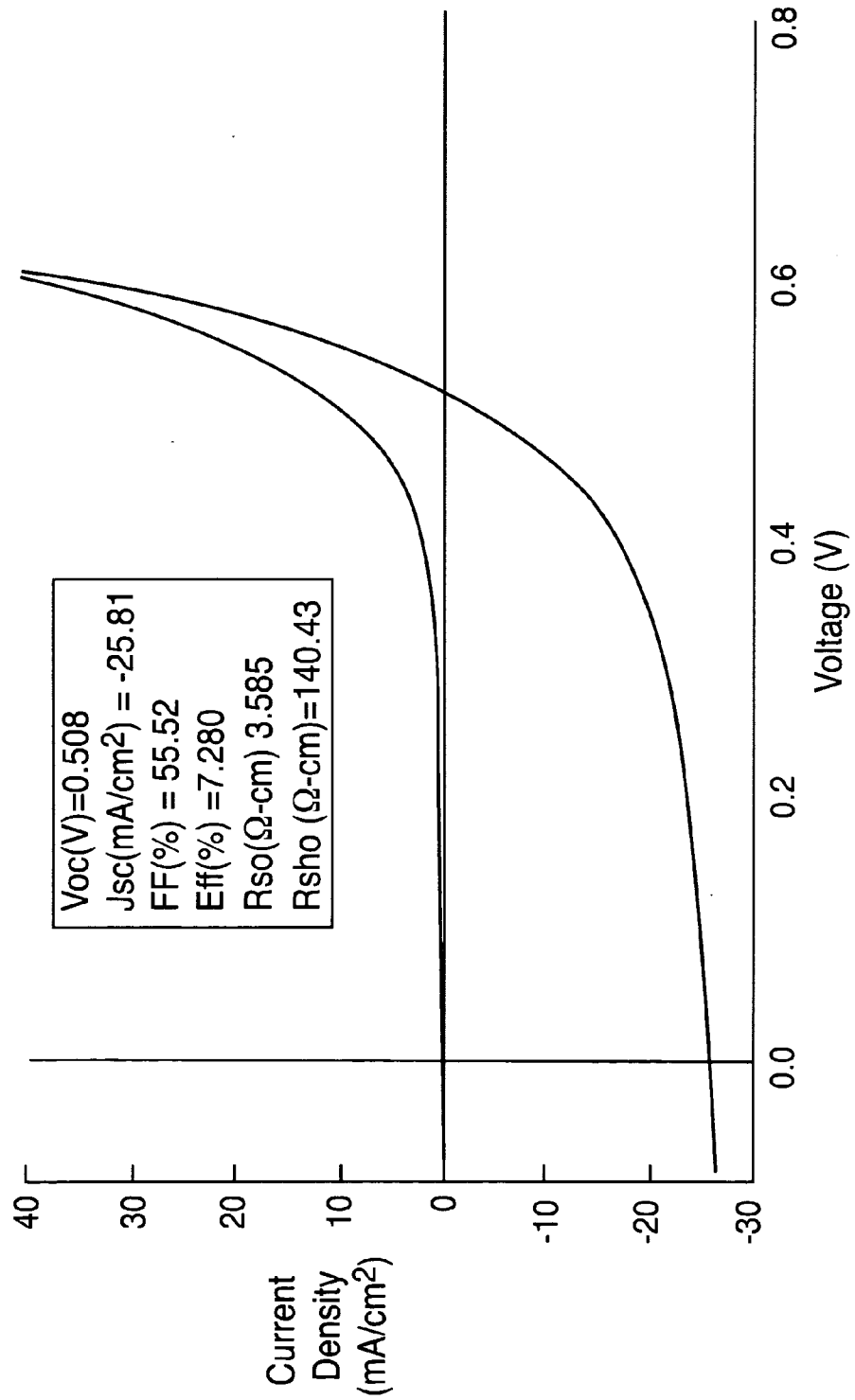
XRD scan of the stacked glass/Mo/In-Ga-Se/Cu-Se precursor film.

FIG. 4



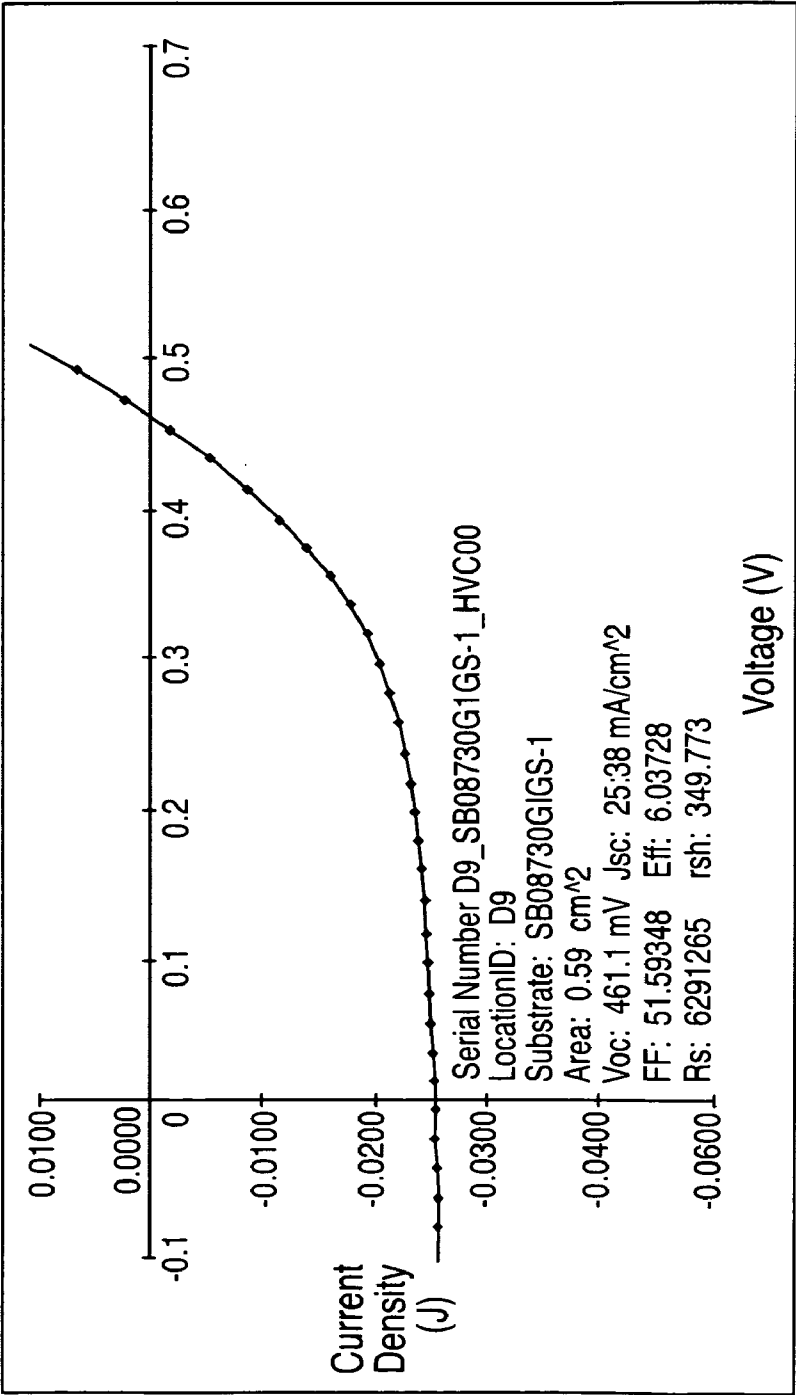
XRD scan of the stacked precursor film after thermal treatment showing conversion to CIGS.

FIG. 5



Device curve obtained from the CIGS film produced in the liquid Cu-Se precursor.

FIG. 6



Device curve obtained from a CIGS film produced using a PVD Cu-Se precursor

FIG. 7



# LIQUID PRECURSOR FOR DEPOSITION OF COPPER SELENIDE AND METHOD OF PREPARING THE SAME

## RELATED APPLICATION

**[0001]** This application claims the benefit of priority from U.S. Provisional Patent Application Ser. No. 61/396,053, entitled "Liquid Precursor for Deposition of Copper Selenide and Method of Preparing the Same," filed May 21, 2010.

## CONTRACTUAL ORIGIN

**[0002]** The United States Government has rights in this invention under Contract No. DE-AC36-08GO28308 between the United States Department of Energy and the Alliance for Sustainable Energy, LLC, the Manager and Operator of the National Renewable Energy Laboratory.

## BACKGROUND

**[0003]** Compounds of Groups IB, IIIA and VIA, especially copper indium diselenide (CIS) and copper indium gallium diselenide (CIGS), have been studied as semiconductor materials for a number of thin-film semiconductor applications. One key application is their use as light absorbing materials in solar cell components. The elements which form these compounds are relatively common and fairly inexpensive, and when formulated and processed into light absorbing materials (e.g., CIS and CIGS), they are highly efficient in converting solar energy to electrical energy.

**[0004]** Unfortunately, cost effective methods of fabricating these light absorbing materials, especially in the form of thin films have been elusive and limited at best. Most current fabrication methods of light absorbing materials (e.g., CIS and CIGS) rely on vacuum deposition techniques (e.g., physical vapor deposition), which are generally expensive and labor-intensive.

**[0005]** Recent advances in the thin film technology involve the use of liquid precursors to deposit precursors of light absorbing materials. Liquid precursors for use in thin film deposition represent less expensive alternatives to vacuum deposition technology. Liquid precursors provide distinct advantages over conventional vacuum deposition technology including higher throughput, lower cost and more efficient material utilization. In addition, liquid precursors are compatible with a broader range of substrate types and surface morphologies including very large substrates or those having considerable flexibility.

**[0006]** Liquid precursors are generally formulated to contain a combination of metal and a multinary chalcogenide material each selected, respectively, from the elements of Group IB, Group IIIA and Group VIA, utilizing hydrazine as a solvent. Upon deposition, the liquid precursor converts into a desired solid precursor or a metal chalcogenide through the application of heat. The deposited solid precursor can then be processed via suitable means in combination with other solid precursors to produce the final light absorbing material (e.g., CIS and CIGS).

**[0007]** The use of hydrazine as a solvent is problematic. Hydrazine is a volatile, corrosive liquid that is expensive, highly toxic and dangerously unstable. Its use therefore is strictly controlled. For the same reasons, hydrazine-containing liquid precursors require special care and handling, and

implementation of extensive safety measures. Thus, the cost and difficulty associated with making and using hydrazine-containing liquid precursors is considerably high.

## SUMMARY

**[0008]** The following embodiments and aspects thereof are described and illustrated in conjunction with systems, tools and methods that are meant to be exemplary and illustrative, not limiting in scope. In various embodiments, one or more of the above-described problems have been reduced or eliminated, while other embodiments are directed to other improvements.

**[0009]** An exemplary method of preparing a liquid precursor is disclosed having a copper selenide content defined by the formula  $Cu_xSe_y$ , wherein x and y are each in the range of 1 to 2 wherein  $x+y$  is in the range of 2 to 3. Such liquid precursors are suitable for forming a solid precursor on a substrate, for example, in the form of thin films, which may be used, for example, in semiconductor applications such as the preparation of light absorbing materials for solar cells. The solid precursor is generally formed by heating the liquid precursor to a temperature and for a time sufficient to drive off the liquid components.

**[0010]** The exemplary method produces a liquid precursor in the form of a liquid based material or composition that does not contain hydrazine and can be used in deposition techniques that are easier, more efficient and more cost effective to use than solid based deposition techniques such as vacuum deposition. The exemplary liquid precursors allow for deposition by suitable deposition techniques such as drop coating, dip coating, spin coating, spraying, brushing, air brushing, ink jet application, stamping, printing, pouring, wiping, smearing, spray deposition, slot coating, and other methods of applying liquids to the surface of a substrate. For example, the deposition technique may be spray deposition or slot coating.

**[0011]** The exemplary method eliminates the use of hydrazine as a solvent, thus eliminating all procedures known to be used in handling and removing hydrazine. The resulting liquid precursor is essentially hydrazine-free, thereby greatly enhancing safety and reducing costs of the process of forming the thin films. The exemplary hydrazine-free liquid precursors permit deposition of solid precursors in a safer and more cost effective manner than those, which contain hydrazine. In addition, the exemplary method produces liquid precursors with higher precursor (i.e., copper-selenide) concentration levels, thus reducing the time necessary for generating the solid precursor. The exemplary liquid precursors can be used to form thin films having a desirable copper selenide composition suitable for use in forming CIS or CIGS thin films useful in the fabrication of solar cells.

**[0012]** Accordingly, an exemplary embodiment is directed to a method of preparing a liquid precursor which includes:

**[0013]** reducing elemental selenium with a stoichiometric amount of a nitrogen-containing reducing agent in the presence of a first solvent to yield a preliminary precursor solution; and

**[0014]** combining the preliminary precursor solution with a solution of a copper salt and a second solvent, which may be the same or different than the first solvent, to yield the liquid precursor.

[0015] Another exemplary embodiment is directed to a method of depositing a solid precursor on a substrate, which includes:

[0016] applying a liquid precursor prepared by the exemplary method described above to the substrate; and

[0017] heating the liquid precursor to a temperature and for a time sufficient to yield the deposited solid precursor on the substrate.

[0018] In another exemplary embodiment, there is provided a liquid precursor which includes:

[0019] a hydrazine-free solvent for a solute comprising copper and selenium; and

[0020] a solute comprising copper and selenium.

[0021] In addition to the exemplary aspects and embodiments described above, further aspects and embodiments will become apparent by reference to the drawings and by study of the following descriptions.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0022] Exemplary embodiments are illustrated in referenced figures of the drawings. It is intended that the embodiments and figures disclosed herein are to be considered illustrative rather than limiting.

[0023] FIG. 1 is a schematic view of chemical reaction steps of an exemplary embodiment of a method for preparing a liquid precursor;

[0024] FIG. 2 is a trace view of atomic percent of copper and selenium as a function of processing temperature for a given time, representing exemplary embodiments;

[0025] FIG. 3 is a trace view of an X-ray diffraction pattern representing an exemplary embodiment of a Cu—Se film dropcast on glass at 200° C.;

[0026] FIG. 4 is a trace view of an X-ray diffraction pattern representing an exemplary embodiment of a precursor film comprising layers of In—Ga—Se and Cu—Se supported on molybdenum and glass prior to thermal treatment;

[0027] FIG. 5 is a trace view of an X-ray diffraction pattern representing an exemplary embodiment of a CIGS film formed after thermal treatment of the precursor film of FIG. 4;

[0028] FIG. 6 is a trace view of a current-voltage (I-V) curve under illumination showing the performance characteristics of a photovoltaic device utilizing a CIGS film produced from a Cu—Se liquid precursor representing an exemplary embodiment; and

[0029] FIG. 7 is a trace view of a current-voltage (I-V) curve under illumination showing the performance characteristics of a photovoltaic device utilizing a CIGS film produced from a Cu—Se precursor deposited through physical vapor deposition (PVD).

#### DETAILED DESCRIPTION

[0030] An exemplary liquid precursor and method of preparing the same is disclosed which is suitable for depositing a desired chemical species or precursor (i.e., copper selenide) on a substrate. The deposited desired chemical species can then be heated to remove volatile components including solvent to yield a solid precursor, for example, in the form of a thin film. The solid precursor of the desired chemical species can be used in forming a CIS (copper-indium-selenide) and/or CIGS (copper-indium/gallium-diselenide) light absorbing material for solar cells.

[0031] The liquid precursor of one exemplary embodiment does not employ hydrazine as a solvent. Accordingly, there is no hydrazine present in the liquid precursor and therefore special efforts to handle and remove hydrazine are eliminated. The exemplary liquid precursor comprises a molar ratio of Cu:Se of about 1:3. Typically, most of the selenium is associated with the copper while a minor portion of selenium will be present in elemental form. The liquid precursor exhibits a relatively high concentration level of copper and selenium suitable for rapidly depositing a thin film on a substrate. The copper concentration in this liquid precursor is in the range of from about 0.08 M to about 0.10 M, whereas prior art liquid precursors with hydrazine as a solvent typically have a copper concentration of from 0.02 M to 0.04 M.

[0032] Copper selenide-containing thin films are useful in the fabrication of CIS and/or CIGS light absorbing materials for solar cells. The copper selenide layer and the indium and/or gallium selenide layer(s) are placed into contact under reactive conditions including heat to form a desirable light absorbing material. An exemplary form of copper selenide for the light absorbing material is CuSe and/or CuSe<sub>2</sub>. During heating to form the light absorbing material the amount and duration of heat can be tailored to control the molar ratio of Cu:Se. One such example is disclosed in U.S. patent application Ser. No. 12/658,204, filed Feb. 4, 2010, incorporated herein by reference. Still other examples are also contemplated.

[0033] In an exemplary embodiment, there is provided a method of preparing a liquid precursor composition having a desirable copper selenide content. The liquid precursor can be applied to a substrate such as glass and simultaneously thermally treated in a manner which provides a solid precursor, for example, in the form of a thin film, having a target copper selenide content as described above. The Cu:Se ratio may be determined by any suitable chemical analysis technique such as, for example, inductively coupled plasma atomic emission spectroscopy (ICP-AES).

[0034] An exemplary method for preparing one exemplary embodiment of the liquid precursor is represented in FIG. 1. The exemplary method involves reducing elemental selenium with a stoichiometric amount of nitrogen-containing reducing agent, such as hydrazine, in the presence of a first solvent (excluding hydrazine) to yield a preliminary precursor solution, and combining the preliminary precursor solution with a solution of a copper salt and a second solvent (excluding hydrazine) to yield the liquid precursor as indicated by equations (1) and (2), respectively. Typically, any precipitate formed during the combining step is separated from the liquid precursor as indicated by equation (3). The precipitate may be separated from the liquid precursor by any suitable separation technique including, but not limited to, filtration, and centrifugation.

[0035] The term “nitrogen-containing reducing agent” is intended to refer to a chemical compound, typically containing nitrogen, which exhibits a standard reduction potential less than the standard reduction potential of selenium, and which is consumed in the oxidation-reduction reaction with selenium to yield by-products which do not adversely affect the reducing reaction and are relatively harmless from an environmental standpoint. An exemplary example of the nitrogen-containing reducing agent is hydrazine.

[0036] As discussed above, the nitrogen-containing reducing agent, for example, hydrazine, is used to reduce elemental selenium in the presence of a first solvent to form the prelimi-

nary precursor solution as indicated in equation (1) of FIG. 1. The term "preliminary precursor solution" is intended to refer to the mixture of the reduced elemental selenium and the first solvent prior to mixing with a solution of a copper salt and a second solvent.

**[0037]** The copper salt may be selected from any soluble copper salts including  $\text{Cu}^{+2}$  salts such as, for example, copper chloride, copper bromide, copper iodide, copper acetate, copper formate, copper nitrate, copper trifluoromethanesulfonate, and the like. The first solvent is any solvent which facilitates the reduction reaction of selenium (see Equation 1 of FIG. 1). The second solvent is any solvent which facilitates the reaction shown in Equation 2 of FIG. 1. Examples of the first and second solvents include, but are not limited to, amines including primary and secondary amines, and glycols. Further examples of the first and second solvents include, but are not limited to, ethylene diamine, pyridine, ethanolamine, diethylene triamine, and ethylene glycol. The first and second solvents may be the same or different.

**[0038]** The nitrogen-containing reducing agent (e.g., hydrazine) is reacted with elemental selenium in stoichiometric amounts. In the exemplary method, utilizing hydrazine as a reducing agent (not as a solvent) in a stoichiometric amount ensures that hydrazine is completely consumed in the reaction with elemental selenium yielding nitrogen gas.

**[0039]** The preliminary precursor solution is thereafter combined or blended with the solution of the copper salt and the second solvent to yield the liquid precursor as indicated in equation (2) of FIG. 1. As indicated in equation (3) of FIG. 1, any precipitate formed from the reaction of the preliminary precursor solution and the copper salt may be separated from the resulting liquid precursor using conventional separation techniques (e.g., filtration, centrifugation).

**[0040]** In an exemplary method of depositing a solid precursor on a substrate, the resulting exemplary liquid precursor is applied to the substrate under elevated temperature conditions for a time sufficient to remove the solvent and other volatile components. During this thermal process step, the exemplary liquid precursor converts into a solid precursor (i.e., Cu—Se), for example, in the form of a thin film. The selection of a temperature and duration of heating have been determined to control the atomic ratio of copper to selenium when the precursor composition is deposited on the substrate (i.e., the relative amount of Cu and Se in the thin film) as shown in FIG. 2. Relatively low temperatures favor the formation of a selenium rich species ( $\text{CuSe}_2$ ). Relatively higher temperatures favor the formation of the copper rich species ( $\text{Cu}_2\text{Se}$ ). Thus, raising the reaction temperature tends to raise the copper content and lower the selenium content.

**[0041]** For example, deposition of the copper selenide liquid precursor at a temperature of from about  $50^\circ\text{C}$ . to  $275^\circ\text{C}$ ., where about  $200^\circ\text{C}$ . favors formation of  $\text{CuSe}_2$ . If deposition is conducted at about  $275^\circ\text{C}$ . to  $350^\circ\text{C}$ ., e.g., about  $325^\circ\text{C}$ ., the predominant species is  $\text{CuSe}$ . As temperatures rise above about  $350^\circ\text{C}$ ., the copper selenide liquid precursor gradually favors the formation of undesirable  $\text{Cu}_2\text{Se}$ . Accordingly, by controlling the temperature of the deposition process within the temperature range described above, the content of the copper selenide compounds can be precisely controlled.

**[0042]** In the formation of CIS and CIGS absorption layers, copper selenide layers containing substantially pure  $\text{CuSe}$  may be used. Accordingly, an exemplary method of forming

a CIS or CIGS absorption layer is to deposit the copper selenide layer at a temperature from about  $100^\circ\text{C}$ . to  $350^\circ\text{C}$ ., for example, about  $325^\circ\text{C}$ .

**[0043]** The exemplary liquid precursors allow for deposition by suitable deposition techniques such as drop coating, dip coating, spin coating, spraying, brushing, air brushing, ink jet application, stamping, printing, pouring, wiping, smearing, spray deposition, slot coating, and other methods of applying liquids to the surface of a substrate. For example, the deposition technique may be spray deposition or slot coating.

**[0044]** In an exemplary embodiment, the liquid precursor can be deposited in a single step heat treating method without resorting to multiple step processes in which the last heating step is rapid thermal processing (RTP). In particular, the liquid precursor may be heated and converted directly to the desirable copper selenide species as the liquid precursor is deposited on the substrate.

**[0045]** Rapid thermal processing (RTP) is defined herein as a heating regimen in which the target film is heated to a desired temperature in a short time, e.g., no more than about 10 minutes. The desired temperature is maintained until the heating process is completed.

**[0046]** In a further exemplary method of depositing a solid precursor on a substrate, the exemplary liquid precursor may be deposited on the substrate to form a solid precursor in the form of a thin film. Thereafter, the deposited liquid precursor is annealed at elevated temperatures to yield a copper selenide film containing  $\text{CuSe}_2$  as the predominant species. In the exemplary method, heating may be conducted while the exemplary liquid precursor is being deposited on the substrate in a single step process.

**[0047]** It will be understood that the one step heating process is exemplary and not required. Thus, the liquid precursor described herein may be initially deposited on a substrate at relatively low temperatures and thereafter treated at higher temperatures including rapid thermal processing.

**[0048]** The Cu—Se containing liquid precursor representing an embodiment makes efficient use of selenium and in an exemplary embodiment obviates the need for multiple heating steps. Because Cu—Se is produced in a relatively pure form, the liquid precursors can be used effectively to facilitate the formation of, for example, CIS or CIGS with large crystal grains in a solid state reaction with In—Se and optional Ga—Se.

**[0049]** In reference to FIG. 3, an exemplary embodiment of the present copper selenide liquid precursor was dropcast on a glass substrate at about  $200^\circ\text{C}$ . and the resulting film was characterized by X-ray diffraction. The X-ray diffraction pattern of the film deposited at about  $200^\circ\text{C}$ . shows a number of peaks identifying crystalline phases of  $\text{CuSe}_2$  and Se.

**[0050]** In reference to FIG. 4, an exemplary embodiment of the present copper selenide liquid precursor was spray deposited at about  $100^\circ\text{C}$ . on a layer of indium, gallium and selenium to yield a stacked precursor film of In—Ga—Se and Cu—Se. The stacked precursor film overlays a layer of molybdenum supported on a glass substrate. The stacked precursor film is characterized by the X-ray diffraction pattern as shown in FIG. 4. The stacked precursor film was heat treated or annealed to convert the film into a CIGS light absorbing material. In reference to FIG. 5, the X-ray diffraction pattern confirms the formation of the CIGS light absorbing material from the stacked precursor film.

[0051] In reference to FIG. 6, the CIGS light absorbing material was incorporated into a solar cell device through the addition of layers of cadmium sulfide and zinc oxide and metal contacts. The solar devices were tested using a solar simulator under 1.5 AMU illumination. Contact probes were placed on the front metal contacts and the back contact of molybdenum. The current was measured while performing a voltage sweep via the contact probes. From the resulting data, the amount of applied voltage required to stop the current flow, or open circuit voltage ( $V_{oc}$ ), the current flow when no voltage is applied, or short circuit current, were determined. The short circuit current density ( $J_{sc}$ ) was calculated from the measured short circuit current and the surface area of the device. The device efficiency is related to the fill factor (FF), which is determined from the sharpness of the device curve where a right angle indicates 100% FF. The device efficiency can be determined from the product of the values of the  $V_{oc}$ ,  $J_{sc}$  and FF.

[0052] The data as shown in FIG. 6 indicates the performance characteristics of a solar cell device fabricated with the present Cu—Se liquid precursor. The data as shown in FIG. 7 indicates the performance characteristics of a solar cell device fabricated with Cu—Se precursor deposited via physical vapor deposition. A comparison of the performance characteristics of FIGS. 6 and 7 show that the solar cell device fabricated with the present Cu—Se liquid precursor exhibited better efficiency than the PVD Cu—Se-based solar cell device.

#### EXAMPLES

[0053] Specific embodiments will now be further described by the following, nonlimiting examples which will serve to illustrate in some detail various features. The following examples are included to facilitate an understanding of ways in which an embodiment may be practiced. It should be appreciated that the examples, which follow represent embodiments discovered to function well in practice. However, it should be appreciated that many changes can be made in the exemplary embodiments which are disclosed while still obtaining like or similar results without departing from the spirit and scope of the claims. Accordingly, the examples should not be construed as limiting the scope of the claims.

##### Example 1

[0054] A solution of selenium in ethylene diamine was prepared by placing selenium powder (2.38 g, 0.030 mole) and ethylene diamine (40 mL) in a flask under a nitrogen atmosphere and adding anhydrous hydrazine (0.160 g, 0.005 mole). The resulting red solution was added over a 45 min period to a stirred solution of copper formate (1.54 g, 0.010 mole) in 40 mL of pyridine to produce a dark red solution containing a small amount of solid precipitate. The precipitate was removed by filtration and the composition of the precursor solution was measured using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The precursor composition found was 25.4 atomic % Cu and 74.6 atomic % Se (Se/Cu=2.94). The precursor solution was spray deposited on a glass substrate at 250° C. and the composition of the resulting film was determined by X-ray fluorescence (XRF). The composition found was 33 atomic % Cu and 66 atomic % Se (Se/Cu=2.0).

[0055] Similar results were obtained when copper formate was dissolved in ethylene diamine or ethanolamine in place of pyridine.

##### Example 2

[0056] A solution of copper nitrate (1.21 g, 0.005 mole) in ethylene diamine was prepared by adding 20 mL of ethylene diamine slowly to the solid in a flask under nitrogen atmosphere. This was added to a solution of selenium in ethylene diamine prepared as described in Example 1 from 0.79 g Se (0.010 mole), 20 mL ethylene diamine and 0.080 g hydrazine (0.0025 mole), resulting in a dark red solution with a small amount of precipitate. The precipitate was removed by filtration and the composition of the precursor solution was measured using ICP-AES. The precursor composition found was 25.6 atomic % Cu and 74.4 atomic % Se (Se/Cu=2.91).

##### Example 3

[0057] A solution of selenium in ethylene diamine was prepared as described in Example 1 from 2.38 g Se (0.030 mole), 40 mL ethylene diamine and 0.160 g hydrazine (0.005 mole) and added to a solution of copper chloride (1.70 g, 0.010 mole) in ethylene diamine (40 mL) and water (1 mL) over a period of 30 min. The solution turned dark red and a small amount of precipitate formed. The precipitate was removed by filtration.

##### Example 4

[0058] A solution of copper trifluoromethanesulfonate (1.10 g, 0.005 mole) in ethylene diamine was prepared by adding 20 mL of ethylene diamine slowly to the solid in a flask under nitrogen atmosphere. This was added to a solution of selenium in ethylene diamine prepared as described in Example 1 from 0.79 g Se (0.010 mole), 30 mL ethylene diamine and 0.080 g hydrazine (0.0025 mole), resulting in a dark red solution with a small amount of precipitate. The precipitate was removed by filtration.

[0059] While a number of exemplary aspects and embodiments have been discussed above, those of skill in the art will recognize certain modifications, permutations, additions, and sub-combinations thereof. It is therefore not intended that the following appended claims and claims hereafter introduced and interpreted to include all such modifications, permutations, additions, and sub-combinations as are within their true spirit and scope.

What is claimed is:

1. A method of preparing a liquid precursor, said method comprising the steps:

reducing elemental selenium with a stoichiometric amount of a nitrogen-containing reducing agent in the presence of a first solvent to yield a preliminary precursor solution; and  
combining the preliminary precursor solution with a solution of a copper salt and a second solvent, which may be the same or different than the first solvent, to yield the liquid precursor.

2. The method of claim 1 wherein the nitrogen-containing reducing agent having a standard reduction potential less than the standard reduction potential of selenium.

3. The method of claim 1 wherein the nitrogen-containing reducing agent is hydrazine.

4. The method of claim 1 wherein the first and second solvents are each selected from the group consisting of primary amines, secondary amines, glycols and combinations thereof.

5. The method of claim 1 wherein the first and second solvents are each selected from the group consisting of ethylene diamine, pyridine, ethanolamine, diethylene triamine, ethylene glycol, and combinations thereof.

6. The method of claim 5 wherein the first and second solvents are ethylene diamine.

7. The method of claim 1 wherein the copper salt is selected from the group consisting of copper chloride, copper bromide, copper iodide, copper acetate, copper formate, copper nitrate, copper trifluoromethanesulfonate, and combinations thereof.

9. The method of claim 1 further comprising the step of separating any precipitate formed during the combining step.

10. The method of claim 9 wherein the separation step is carried out using a process selected from the group consisting of filtration, centrifugation, and combinations thereof.

11. The method of claim 1 wherein the liquid precursor comprises a copper concentration of from about 0.08 M to 0.10 M.

12. A method of depositing a solid precursor on a substrate, said method comprising the steps of:

applying the liquid precursor prepared by the method of claim 1 to the substrate; and

heating the liquid precursor to a temperature and for a time sufficient to yield the deposited solid precursor on the substrate.

13. The method of claim 12 wherein the deposited solid precursor is a thin film.

14. The method of claim 12 wherein the temperature is at least 50° C.

15. The method of claim 14 wherein the temperature is from about 50° C. to about 275° C.

16. The method of claim 12 wherein the deposited solid precursor is copper selenide at least substantially in the form of CuSe<sub>2</sub>.

17. The method of claim 12 wherein the deposited solid precursor comprises elemental selenium.

18. The method of claim 12 wherein the deposited solid precursor is characterized by an X-ray diffraction pattern substantially as shown in FIG. 2.

19. The method of claim 12 wherein the applying step is implemented through a process selected from the group consisting of drop coating, dip coating, spin coating, spraying, brushing, air brushing, ink jet application, stamping, printing, pouring, wiping, smearing, spray deposition, slot coating, and combinations thereof.

20. The method of claim 12 wherein the liquid precursor comprises a copper concentration in the range of about 0.08 M to about 0.10 M.

21. A liquid precursor comprising:

a hydrazine-free solvent for a solute comprising copper and selenium; and

a solute comprising copper and selenium.

22. The liquid precursor of claim 21 wherein copper and selenium are present in a molar ratio of about 1:3.

23. The liquid precursor of claim 21 wherein the hydrazine-free solvent comprises solvent selected from glycols, amines, and combinations thereof.

24. The liquid precursor of claim 21 wherein the copper concentration is in the range of about 0.08 M to about 0.10 M.

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