

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
23 February 2012 (23.02.2012)(10) International Publication Number
WO 2012/023973 A2(51) International Patent Classification:
H01L 21/20 (2006.01)(21) International Application Number:
PCT/US2011/001434(22) International Filing Date:
16 August 2011 (16.08.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
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(54) Title: LIQUID PRECURSOR FOR DEPOSITION OF INDIUM SELENIDE AND METHOD OF PREPARING THE SAME

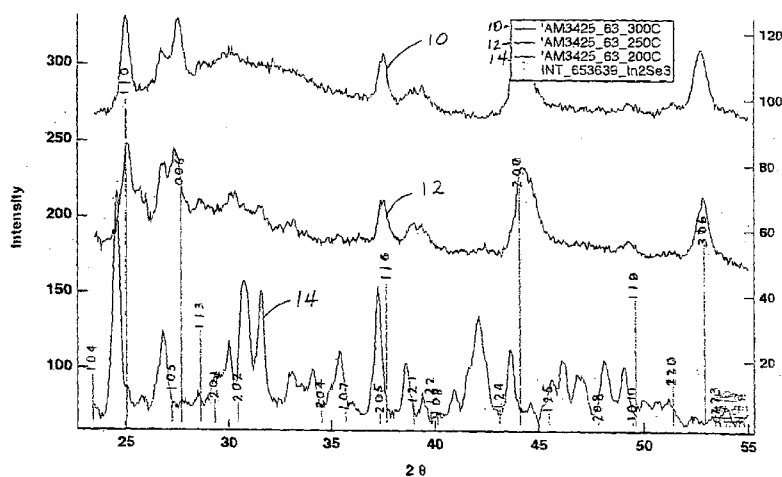


FIG. 2

(57) Abstract: Liquid precursors containing indium 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 method of depositing a liquid precursor on a substrate are also disclosed.



SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG). **Published:**

— *without international search report and to be republished
upon receipt of that report (Rule 48.2(g))*

LIQUID PRECURSOR FOR DEPOSITION OF INDIUM SELENIDE
AND METHOD OF PREPARING THE SAME

5

CONTRACTUAL ORIGIN

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
10 Renewable Energy Laboratory.

RELATED APPLICATION

The present Application is related to and takes priority from U.S. Provisional
15 Application Serial No. 61/401,607, filed August 16, 2010, the teachings of which are incorporated herein by reference to the extent they do not conflict herewith.

BACKGROUND

20

Compounds of Groups IB, IIIA and VIA, including for example 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 into electrical energy.

5 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.

10

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
15 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.

20 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 to a desired solid precursor or a metal

chalcogenide through the application of heat. The deposited solid precursor can then be processed through suitable means in combination with other solid precursors to produce the final light absorbing material (e.g., CIS and CIGS).

5 The use of hydrazine as a solvent is problematic. Hydrazine is a volatile, corrosive liquid that is not only highly toxic and dangerously unstable, but also expensive. Its use is therefore strictly controlled. For the same reasons, hydrazine-containing liquid precursors require special care and handling including implementation of extensive safety measures. Thus, the cost and difficulty of making
10 and using hydrazine-containing liquid precursors presents problems in the industry.

SUMMARY

 The following embodiments and aspects thereof are described and illustrated
15 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.

20 An exemplary method of preparing a liquid precursor is disclosed having an indium selenide content defined by the formula In_xSe_y , wherein x and y are each in the range of 1 to 3 and wherein x+y is in the range of 2 to 5. 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.

5

The exemplary method produces a liquid precursor starting from elemental selenium 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 than solid based deposition techniques such as vacuum
10 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
15 deposition or slot coating.

The exemplary method eliminates the use of hydrazine entirely or eliminates the use of hydrazine in amounts where it can function as a solvent. Thus, the exemplary method eliminates the necessity of procedures known to be used for
20 handling and removing hydrazine. The resulting liquid precursor is essentially hydrazine-free, thereby greatly enhancing safety and further reducing costs associated with the process for depositing a solid precursor on a substrate. 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 elevated precursor (i.e., indium-selenide) concentration levels, thus reducing the time necessary to generate the solid precursor. The exemplary liquid precursors can be used to form
5 thin films having a desirable indium selenide composition suitable for use in forming CIS or CIGS thin films useful in the fabrication of solar cells.

Accordingly, an exemplary embodiment is directed to a method of preparing a liquid precursor which includes: contacting elemental selenium with an amount of at
10 least one nitrogen-containing agent effective to yield a preliminary precursor solution; and combining the preliminary precursor solution with a solution of an indium salt and a solvent for the indium salt to yield the liquid precursor. In one such exemplary embodiment, hydrazine is not used as the nitrogen-containing agent. In another such exemplary embodiment, hydrazine is used as a nitrogen containing agent but in
15 a controlled amount (e.g. stoichiometric amount) wherein hydrazine acts as a reducing agent and is essentially consumed by its reaction with elemental selenium. In this exemplary embodiment, a solvent may be used for the reaction. The exemplary embodiment encompasses the use of other reducing agents, as a replacement for hydrazine, which can reduce elemental selenium as shown by the
20 chemical reaction represented in Figure 1.

Another exemplary embodiment is directed to a method of depositing a solid precursor on a substrate, which includes applying a liquid precursor prepared by the

exemplary method described above 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.

- 5 In another exemplary embodiment, there is provided a liquid precursor which includes a hydrazine-free solvent for a solute comprising indium and selenium; and a solute comprising indium and selenium.

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

BRIEF DESCRIPTION OF THE DRAWINGS

- 15 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.

 Figure 1 is a schematic view of a chemical reaction of an embodiment for
20 forming a liquid precursor;

Figure 2 is a trace view of X-ray diffraction patterns, representing three embodiments in which dropcast In-Se films were prepared at 200°C, 250°C and 300°C, respectively; and

5 Figure 3 is a trace view of a thermogravimetric analysis characterization of changes in weight in relation to change in temperature of the In-Se liquid precursor for one embodiment.

DETAILED DESCRIPTION

10

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., indium selenide) on a substrate. The deposited chemical species can then be heated to remove volatile components including any solvent which may be present to yield a
15 solid precursor, for example, in the form of a thin film. The solid precursor of the desired chemical species can be used to form CIS (copper-indium-selenide) and/or CIGS (copper-indium/gallium-diselenide) light absorbing materials for solar cells.

The liquid precursor of one exemplary embodiment utilizes at least one
20 nitrogen-containing agent which may act as a reducing agent and/or a solvent to form a selenium containing solution. When hydrazine is used as a nitrogen-containing agent, the amount (e.g. a stoichiometric amount) which is employed to form the preliminary precursor solution is sufficient to reduce up to 50% of the

elemental selenium. Excess hydrazine is avoided so that hydrazine is not present in the liquid precursor.

When hydrazine is used and functions as a reducing agent, it is desirable to
5 conduct the method in the presence of at least one additional nitrogen-containing agent and optionally in the presence of a non-nitrogen containing solvent such as glycol.

In another exemplary embodiment, hydrazine is omitted from the process and
10 a suitable solvent such as ethylene diamine is used in solvent functioning amounts (i.e. greater than a stoichiometric amount) to dissolve the elemental selenium to form the preliminary precursor solution.

As indicated above, the liquid precursor of one exemplary embodiment does
15 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.

In another exemplary embodiment, hydrazine is used but not in solvent
20 functioning amounts. Instead, hydrazine is used in an amount only sufficient to reduce a portion of the elemental selenium (e.g. up to 50%). As a result, the hydrazine is converted to relatively harmless byproducts as represented in the

reaction shown in Figure 1. In yet another exemplary embodiment, selenium is reduced but not by hydrazine.

The exemplary liquid precursor comprises a molar ratio of In:Se of about 1:1 to 2:3. Typically, most of the selenium is associated with indium while a minor portion of selenium will be present in elemental form. The exemplary liquid precursor exhibits a relatively high concentration level of indium and selenium suitable for rapidly depositing a solid precursor, for example, in the form of a thin film, on a substrate. The indium concentration in the exemplary liquid precursor is in the range of about 0.10 M to about 0.50 M, whereas prior art liquid precursors with hydrazine added in solvent functioning amounts typically have an indium concentration of from about 0.02 M to about 0.04 M.

Indium selenide-containing depositions, for example, in the form of a thin film, are useful in the fabrication of CIS and/or CIGS light absorbing materials for solar cells. The indium selenide layer and the copper and/or gallium selenide layer(s) are placed in contact under reactive conditions including heat to form a desirable light absorbing material. An exemplary form of indium selenide for the light absorbing material is InSe and/or In_2Se_3 . During heating to form the light absorbing material the amount and duration of heat can be tailored to control the molar ratio of In:Se. Still other examples are also contemplated.

In an exemplary embodiment, there is provided a method of preparing a liquid precursor or precursor composition having a desirable indium selenide content. The exemplary 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 indium selenide content as described above. The In:Se ratio may be determined by any suitable chemical analysis technique, such as, for example, inductively coupled plasma atomic emission spectroscopy (ICP-AES) or X-ray fluorescence spectroscopy (XRF).

An exemplary method for preparing one exemplary embodiment of the liquid precursor is represented in Figure 1. The exemplary method involves reducing elemental selenium with a stoichiometric amount of a nitrogen-containing reducing agent such as, for example, hydrazine, in the presence of a solvent (excluding hydrazine) to yield a preliminary precursor solution, and combining the preliminary precursor solution with a solution of an indium salt and a solvent for the indium salt (excluding hydrazine) to yield the liquid precursor in the form of a suspension of small particles, as indicated in equations (1) and (2), respectively. The solvents used in these methods steps may be the same or different.

The term "nitrogen-containing agent" is intended to refer to a chemical compound containing nitrogen, which either 1) exhibits a standard reduction potential less than the standard reduction potential of selenium (i.e. acts as a reducing agent), and which is consumed in the oxidation-reduction reaction with selenium to yield by-

products which do not adversely affect the reduction reaction and are relatively harmless from an environmental standpoint or 2) functions as a solvent for elemental selenium when used in solvent functioning amounts. An exemplary example of a nitrogen-containing agent which functions as a reducing agent is hydrazine.

- 5 Examples of nitrogen containing agents which may function as solvents include primary and secondary amines such as ethylene diamine.

As discussed above, the nitrogen-containing agent, for example, hydrazine, may be used to reduce elemental selenium in the presence of a solvent to form the preliminary precursor solution as indicated in equation (1) of Figure 1. The term
10 "preliminary precursor solution" is intended to refer to the mixture of the reduced elemental selenium and the solvent prior to mixing with a solution of the indium salt. Because hydrazine is used in controlled amounts to effect reduction, there is virtually no hydrazine present once the elemental selenium has been reduced.

15

The indium salt may be selected from any soluble indium salts including In^{3+} salts such as, indium nitrate, indium chloride, indium triflate, and the like. The solvent used to form the preliminary precursor solution is any solvent which facilitates the conversion (e.g. the reduction reaction) of selenium to solution form
20 (see equation (1) of Figure 1). In the second step of the reaction, the solvent used therein facilitates the dissolution of the indium salt. Examples of compounds that may function as a solvent in the first step include nitrogen-containing agents such as primary and secondary amines as well as non-nitrogen containing compounds such

as glycols. Specific examples of nitrogen-containing agents and solvents used in the first step of the method include, but are not limited to, ethylene diamine, pyridine, ethanolamine, diethylene triamine, N-methylimidazole, and ethylene glycol. The solvent used in the second step of the reaction includes those which facilitate the reaction shown in equation (2) of Figure 1. Examples of these solvents include, but are not limited to, alcohols such as, for example, a lower alkanol preferably having 1-6 carbon atoms (e.g., methanol, ethanol, butanol), water, dimethylformamide as well as those solvents suitable for use in the first step of the method (e.g., glycols such as ethylene glycol or primary and secondary amines such as ethylene diamine).

When the nitrogen-containing agent is a reducing agent (e.g. hydrazine), it is preferably 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.

The preliminary precursor solution is thereafter combined or blended with the solution of the indium salt to yield the liquid precursor as a suspension of small particles as indicated in equation (2) of Figure 1.

In another exemplary embodiment of forming the preliminary precursor solution elemental selenium is dissolved in a suitable solvent. The amount of the solvent must be sufficient to dissolve the elemental selenium and provide the

preliminary precursor solution. Suitable amounts will depend on the particular solvent chosen but will generally be greater than a stoichiometric amount. Examples of such solvents include nitrogen-containing agents such as primary and secondary amines (e.g. ethylene diamine, pyridine, ethanolamine, diethylene triamine, N-methylimidazole and combinations thereof) and glycols (e.g. ethylene glycol).

In an exemplary method of depositing a solid precursor on a substrate, the resulting exemplary liquid precursor suspension is applied to the substrate under elevated temperature conditions sufficient to remove volatile components such as solvent. During this thermal process step, the exemplary liquid precursor suspension converts to a solid precursor (i.e., In-Se), for example, in the form of a thin film. The selection of a heat treating temperature and the duration of the heat treatment have been determined to control the atomic ratio of indium to selenium when the exemplary liquid precursor is deposited on the substrate (i.e., the relative amount of In and Se in the solid precursor). Relatively low temperatures favor the formation of a metal organic containing In and Se. Relatively higher temperatures favor the formation of the species In_2Se_3 (Figure 2).

For example, deposition of the exemplary indium-selenide liquid precursor at a temperature of from about room temperature to 200°C , favors formation of a metal organic compound. If deposition is conducted at a temperature of about 250°C to 300°C , the predominant species is In_2Se_3 .

In the formation of CIS and CIGS absorption layers, indium selenide layers containing substantially pure In_2Se_3 may be used. Accordingly, an exemplary method of forming a CIS or CIGS absorption layer is to deposit the indium selenide layer at a temperature from about 250°C to 300°C.

5

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 include spray deposition or slot coating.

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 indium selenide species as the liquid precursor is deposited on the substrate.

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

In a further exemplary method of depositing a solid precursor on a substrate, the exemplary liquid precursor suspension may be deposited on the substrate to form a solid precursor, for example, in the form of a thin film. Thereafter, the deposited liquid precursor is annealed at elevated temperatures to yield an indium selenide film containing In_2Se_3 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.

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.

The In-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 In-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 Cu-Se and optional Ga-Se.

In reference to Figure 2, three exemplary embodiments of the present solid precursor in the form of a film represented by x-ray diffraction patterns 10, 12, and 14, are shown. The In-Se precursors were each deposited as a suspension in

ethylene diamine and ethylene glycol dropcast on glass substrates at 200°C, 250°C, and 300°C, respectively. The X-ray diffraction pattern 14 of the film deposited at 200°C indicates a number of peaks which do not match with any known In-Se phase and is presumed to be a crystalline form of the corresponding precursor. The films
5 deposited at 250°C and 300°C, respectively, each generated X-ray diffraction patterns 12 and 10, respectively, that correspond to a cubic In_xSe_y phase. It is further noted that the In:Se ratio in the dropcast films was determined through X-ray fluorescence to be 1:1.

10 In reference to Figure 3, the thermal decomposition of the liquid precursor composed of In-Se precursor suspension in ethylene diamine/ethylene glycol mixed solvent, was examined using thermogravimetric analysis (TGA) techniques. The TGA trace in Figure 3 shows loss of solvents in two well defined steps as the deposited liquid precursor converts to the desired stable In-Se precursor at about
15 275°C.

EXAMPLES

Specific embodiments will now be further described by the following, non-
5 limiting 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
10 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

15

A solution of selenium in ethylene diamine was prepared by placing Se
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 indium
20 chloride (3.32 g, 0.015 mole) in 125 mL of pyridine to produce a viscous, dark red
suspension. This precursor suspension was drop cast on glass substrates heated at
300°C. The composition of the film was determined by X-ray fluorescence (XRF).
The composition found was 50 atomic % In and 50 atomic % Se (Se/In=1.0).

Example 2

A solution of selenium in ethylene diamine was prepared by placing Se powder (3.16 g, 0.040 mole) and ethylene diamine (40 mL) in a flask under a nitrogen atmosphere and adding anhydrous hydrazine (0.320 g, 0.010 mole). The resulting red solution was added over a 45 min period to a stirred solution of indium(III) chloride hydrate (11.72 g, 0.040 mole) in 40 mL of ethylene glycol. The exothermic reaction produced an orange suspension that was stable for several days without phase separation. This precursor suspension was dropcast on glass substrates at 200, 250, and 300°C and the XRD traces of the resulting deposits are shown in Figure 2. The composition of the film deposited at 200°C was determined by X-ray fluorescence (XRF). The composition found was 50 atomic % In and 50 atomic % Se (Se/In=1.0).

15

Example 3

A solution of selenium in ethylene diamine was prepared by placing Se powder (0.79 g, 0.010 mole) and ethylene diamine (20 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 indium(III) trifluoromethanesulfonate (2.81 g, 0.005 mole) in 20 mL of ethylene

20

diamine. The exothermic reaction produced a brown solution that was stable for several days without precipitation.

Example 4

5

A solution of selenium in ethylene diamine was prepared by placing Se powder (0.79 g, 0.010 mole) and ethylene diamine (20 mL) in a flask under a nitrogen atmosphere and adding anhydrous hydrazine (0.080 g, 0.0025 mole). The resulting red solution was added over a 45 min period to a stirred solution of
10 indium(III) nitrate hydrate (3.82 g, 0.010 mole) in 20 mL of ethylene glycol. The reaction produced an orange suspension that was stable for several days without phase separation.

Example 5

15

A solution of selenium in ethylene diamine was prepared by placing Se powder (0.79 g, 0.010 mole) and ethylene diamine (40 mL) in a flask under a nitrogen atmosphere and heating the mixture to 120°C for 3 hours, at which point the selenium was completely dissolved to form a red solution. This red solution was
20 added over a 15 minute period to a stirred solution of indium(III) nitrate hydrate (3.82 g, 0.010 mole) in 20 mL of dimethylformamide under a nitrogen atmosphere. The reaction produced an orange solution that was stable for several days without precipitation. This precursor solution was deposited on glass substrates by spray

deposition at a substrate temperature of 200°C. The composition of the resulting film was determined by X-ray fluorescence (XRF). The composition found was 50 atomic % In and 50 atomic % Se (Se/In=1.0).

5 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
10 are within their true spirit and scope.

What Is Claimed Is:

1. A method of preparing a liquid precursor, said method comprising the steps:
5 contacting elemental selenium with an amount of at least one nitrogen-containing agent effective to yield a preliminary precursor solution; and
 combining the preliminary precursor solution with a solution of an indium salt to yield the liquid precursor.
- 10 2. The method of claim 1 wherein the nitrogen-containing agent is selected from the group consisting of hydrazine, primary amines, secondary amines, and combinations thereof.
- 15 3. The method of claim 2 wherein the nitrogen-containing agent is selected from the group consisting of ethylene diamine, pyridine, ethanolamine, diethylene triamine, N-methylimidazole, and combinations thereof.
- 20 4. The method of claim 1 wherein the nitrogen-containing agent reduces the elemental selenium.
5. The method of claim 4 wherein the nitrogen-containing agent reduces up to about 50% of the elemental selenium.

6. The method of claim 1 further comprising conducting the step of contacting the elemental selenium and at least one nitrogen-containing agent in the presence of a non-nitrogen containing solvent.

5 7. The method of claim 6 wherein the non-nitrogen containing solvent is a glycol.

8. The method of claim 1 wherein the solution of indium salt comprises a solvent selected from the group consisting of alcohols, glycols, water, dimethylformamide, primary amines, secondary amines and combinations thereof.

10

9. The method of claim 1 wherein the solvent for the indium salt is selected from the group consisting of methanol, ethanol, butanol, ethylene glycol, dimethylformamide, and combinations thereof.

15 10. The method of claim 1 wherein the indium salt is selected from the group consisting of indium nitrate, indium chloride, indium triflate, and combinations thereof.

11. The method of claim 1 wherein the liquid precursor comprises an indium
20 concentration in the range of about 0.10 M to about 0.50 M.

12. The method of claim 1 wherein the nitrogen-containing agent has a standard reduction potential less than the standard reduction potential of selenium.

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

obtaining a liquid precursor prepared by the following steps:

5 a) contacting elemental selenium with an amount of at least one nitrogen-containing agent effective to yield a preliminary precursor solution; and

 b) combining the preliminary precursor solution with a solution of an indium salt, to yield the liquid precursor;

10 applying the liquid precursor 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.

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

15

15. The method of claim 13 wherein the heating step is conducted at a temperature of at least 250°C.

16. The method of claim 15 wherein the temperature is from about 250°C to about
20 300°C.

17. The method of claim 13 wherein the deposited solid precursor is indium selenide at least substantially in the form of InSe.

18. The method of claim 13 wherein the deposited solid precursor comprises elemental selenium.

5 19. The method of claim 13 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.

10 20. The method of claim 13 wherein the liquid precursor comprises an indium concentration in the range of about 0.10 M to about 0.50 M.

21. A liquid precursor comprising:
a hydrazine-free solvent for a solute comprising indium and selenium; and
15 a solute comprising indium and selenium.

22. The liquid precursor of claim 21 wherein indium and selenium are present in a molar ratio of about 1:1 to 2:3.

20 23. The liquid precursor of claim 21 wherein the hydrazine-free solvent is selected from the group consisting of alcohols, glycols, dimethylformamide, water, primary amines, secondary amines and combinations thereof.

24. The liquid precursor of claim 21 wherein the indium concentration is in the range of about 0.10 M to about 0.50 M.

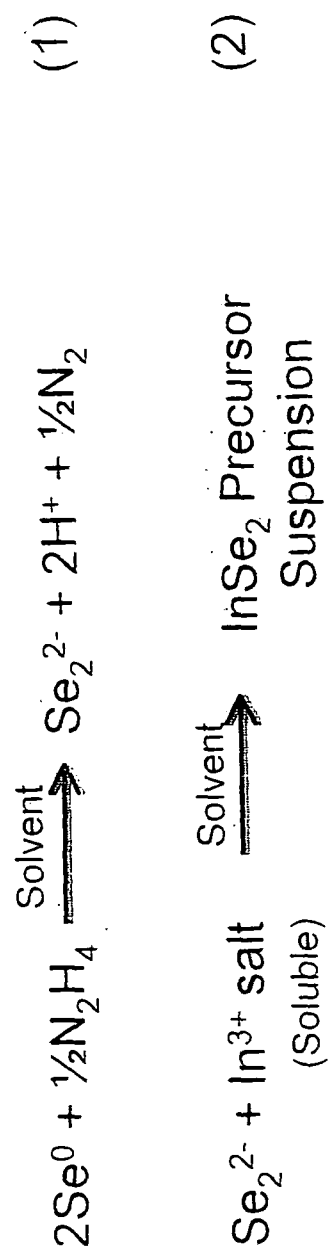


Figure 1

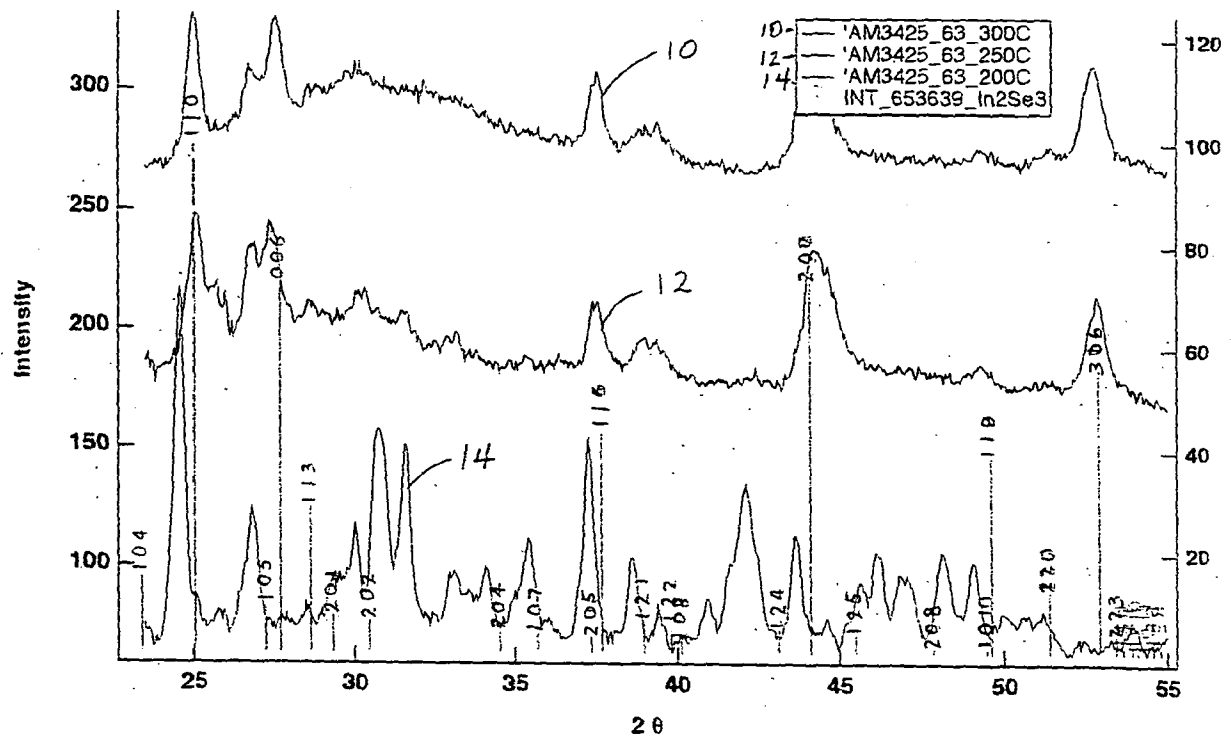


FIG. 2

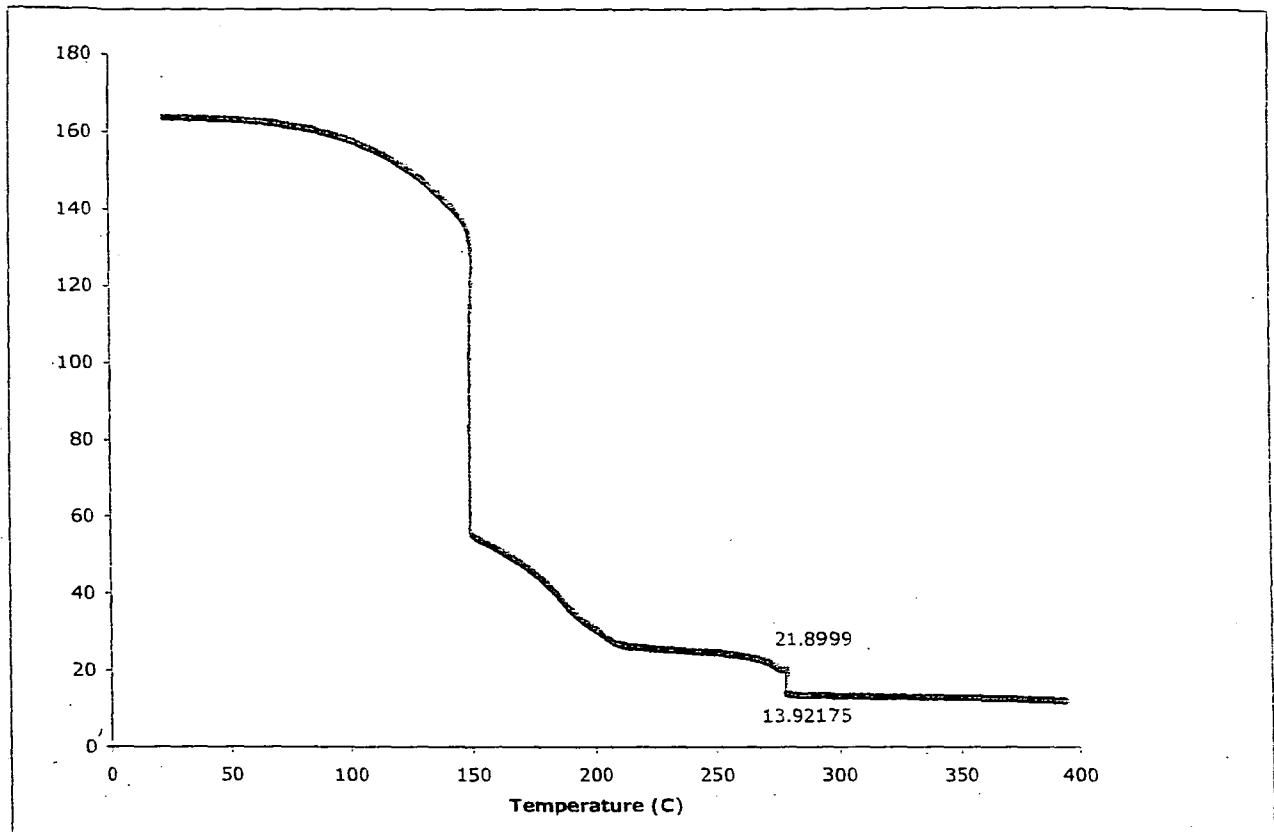


FIG. 3