SINGLE-SOURCE PRECURSORS FOR TERNARY CHALCOPYRITE MATERIALS, AND METHODS OF MAKING AND USING THE SAME

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A single source precursor for depositing ternary I-III-VI$_2$ chalcopyrite materials useful as semiconductors. The single source precursor has the I-III-VI$_2$ stoichiometry “built into” a single precursor molecular structure which degrades on heating or pyrolysis to yield the desired I-III-VI$_2$ ternary chalcopyrite. The single source precursors effectively degrade to yield the ternary chalcopyrite at low temperature, e.g. below 500°C, and are useful to deposit thin film ternary chalcopyrite layers via a spray CVD technique. The ternary single source precursors according to the invention can be used to provide nanocrystalline structures useful as quantum dots. A method of making the ternary single source precursors is also provided.
OTHER PUBLICATIONS


Harris, J.D., et al., “Using Single Source Precursors and Spray Chemical Vapor Deposition to Grow Thin-Film CupInS2”, Proc. of the 28th IEEE Photovoltaics Specialists Conference, 2000, ABSTRACT.


Shibata, J., et al., “Transmission Electron Microscopic Studies of LiNb0.5Ta0.503 Films Deposited on Sapphire Substrates by Thermal Plasma Spray CVD (Microstructure of LiNb0.5Ta0.503 Films Deposited by Thermal Plasma Spray CVD)”, Materials Transactions, 2002, 43(7), pp. 1517-1524.
* cited by examiner
Figure 7

- mA/cm²
- Voltage (V)

- annealed
- as deposited
Figure 9

\[(\alpha \cdot h \nu)^2 \times 10^8 \text{(cm}^2\text{eV)}^2\]

- Annealed, 600 °C, 10min, N\textsubscript{2}
- As deposited, 400 °C
Figure 15

Intensity (arbitrary units)

2-Theta (deg)
STATEMENT OF GOVERNMENT SPONSORED RESEARCH

The U.S. Government has a paid-up license in this invention and the right in limited circumstances to require the patent owner to license others on reasonable terms as provided for by the terms of Contract Nos. NCC3-947, NCC3-817, NCC3-563, NCC3-958 and NCC3-734, all awarded by the National Aeronautics and Space Administration (Glenn Research Center, Cleveland, Ohio). This invention was made with Government support under contract Nos. NCC3-947, NCC3-817, NCC3-563, NCC3-958 and NCC3-734, all awarded by the National Aeronautics and Space Administration (Glenn Research Center, Cleveland, Ohio). The Government has certain rights in this invention.

BACKGROUND OF THE INVENTION

The development of thin film flexible lightweight solar cells is of high importance for both terrestrial and space applications. Thin film solar cells use 100-100 times less semiconducting material and are less expensive to manufacture than conventional crystalline silicon solar cells. In addition, the use of toxic reagents is a limiting factor. The use of multi-source inorganic/organometallic precursors, electrodeposition, reactive-sintering, and flash evaporation, developed based on the ternary chalcopyrite absorber layers, (I-111-VI,; Cu(In:Ga)(S:Se),) have been the focus of intense investigation. The use of chalcopyrite absorbers are highly appealing since their band gaps correlate well to the maximum photon density in the solar spectrum for both terrestrial (air mass of 1.5 [AM1.5]), and spectrum for both terrestrial (air mass of 1.5 [AM1.5]), and current methods for depositing ternary crystalline compounds include co-evaporation of multi-source precursors, electrodeposition, reactive-sintering, and flash evaporation, which are often followed by toxic sulfurization/selenization steps at elevated temperatures such as 800° C. Furthermore, under these conditions loss of volatile In/Ga chalcogenides is common. The high temperature requirements of the above methods makes them incompatible with all presently known flexible polyimides, and other polymer substrates. In addition, the use of toxic reagents is a limiting factor.

The use of multi-source single sources inorganometallic precursors in a CVD type process is more appealing due to milder process parameters. However, stoichiometric control of deposited films can be difficult to achieve and film contamination has been reported.

Recently, the synthesis and use of a ternary single source precursor (SSP) having the I-III-II stoichiometry "built in" has been investigated. In 1993, Hirpo and coworkers synthesized [(PP3)2Cu(SEt)2In(SEt)2], the first known SSP for a ternary I-III-II chalcopyrite material, in this case (CuInS2). Wakgari Hirpo et al, Synthesis of Mixed Copper-Indium Chalcopyrates. Single-Source Precursors for the Photovoltaic Materials CuInSe2, (Q=S, Se), J. Am. Chem. Soc. 1993, 115, 1597-1599. The preparation of heteromultinuclear complexes was also reported in the same work. The complexes consisted of tetrahedrally arranged Cu and In centers, with two bridging thiolate and selenolate groups [Eq. 1].

\[
[\text{Eq. 1}]
\]

Pyrolysis studies undertaken revealed that the Se derivative could be converted into CuInSe2 at 400-450° C @ 0.01 mm Hg [Eq.2], but none of the precursors had been evaluated in a thin-film deposition study.

In early studies Nomura et al. reported that an equimolar mixture of [Bu'In(SPr)2] and [Cu(S,SCNBu r)2] decomposed to afford CuInS2 powders. Nomura, R.; Kanaya, K.; Matsuda, H., Preparation of Copper-Indium-Sulfide thin films by solution Pyrolysis of organometalllic sources, Chem. Let., 1988, 1849-1850. On this basis, solution pyrolysis of this mixture dissolved in o-xylene was used to deposit thin-film CuInS2 at 350° C and low pressure onto glass substrates. Film composition was determined by XRD, which showed broad peaks. XRD revealed the ratios of In/Cu and Cu/Cu decreased with temperature, and a second phase to be present for films deposited at 350° C. Grain size was estimated to be in the range of 50-100 nm as determined by SEM. It was later realized that the equimolar reaction mixture of [Bu'In(SPr)2] and [Cu(S,SCNBu r)2] decomposed to afford the single source precursor [Bu'ln(SPr)2Cu(S,SCNPr)2] before decomposing to the chalcopyrite matrix. Analytical and spectral data confirmed that the mixture of [Bu'In(SPr)2] and [Cu(S,SCNBu r)2] yielded the above SSP. However, the SSP itself was synthesized in situ as an intermediate to the desired ternary chalcopyrite material starting from the two reagents [Bu'In(SPr)2] and [Cu(S,SCNBu r)2] which must be combined in equimolar ratios. A number of analogous ternary CIS precursors were also synthesized by the reaction of alkyl indium thiols with copper dithiocarbamates [Eq.3].

2In(SPr)2 + 2Cu(S,SCNR)2 → [2In(SPr)2Cu (S,SCNR)2] + (R2NCS)2

However, only [Bu'In(SPr)2Cu(S,SCNPr)2] was successfully implemented for depositing pure CuInS2 by low pressure MOCVD. In the case of [BuIn(SPr)2Cu(S,SCNPr)2], tetragonal CuInS2 was deposited [Eq.4].

\[
[\text{Eq. 4}]
\]
Spray CVD of Copper Indium Difluoride Films: Control of Microstructure and Crystallographic Orientation. Chem Vap. Deposition, 1999, 5, 105-108; Hollingsworth, J. A., Buhro, W. E., Hepp, A. F., Jenkins, P. P., Stan, M. A., W. E., Hepp, A. F., Jenkins, P. P., Stan, M. A., particles of 5 & 200 nm resident on top. At higher deposition temperatures (>500 “C.), CuInS₂ phase thin films were deposited. The morphology of the deposited thin films was found to be temperature dependent. During the course of the study, the morphology of the deposited thin films was controlled by varying the temperature and carrier solvent. Single phase 112 orientated CuInS₂ thin films were deposited from the carrier solvent. Single phase 112 orientated CuInS₂ thin films were deposited. RBS EDS and XPS analysis showed that the films were direct band gap semiconductors.

**SUMMARY OF THE INVENTION**

A single source precursor for the deposition of ternary chalcopyrite materials is provided. The single source precursor has the empirical formula [{L}, M'(ER)x, M''(ER)y, L-]{L}, M'(ER)x, M''(ER)y}, wherein x is 1–4, x+y+z=4, L is a Lewis base that is coordinated to M’ via a dative bond, n is greater than or equal to 1, M’ is a Group I-B atom, M” is a Group III-A atom, E is a Group VI-A atom, X is a Group VII-A atom, and each R is selected from the group consisting of alkyl, aryl, vinyl, perfluoro alkyl, perfluoro aryl, silane, and carbamate groups, said single source precursor excluding {P(C₆H₅)₃, Cu(SEt), In(SEt)} at a temperature of 400 “C., the films consisted of more angular and uniform grain size of approx 200 to 400 nm. Photoluminescence (PL) data and optical transmission measurements confirmed the deposited CuInS₂ thin films were direct band gap semiconductors.

**BRIEF DESCRIPTION OF THE DRAWINGS**

The patent or application file contains at least one drawing executed in color. Copies of this patent or patent application publication with color drawing(s) will be provided by the Office upon request and payment of the necessary fee.

FIG. 1 is a single crystal X-ray resolved structure of a new SSP, [{P(PPh₃)₃, Ag(SMe)₂, In(SMe)₂}], according to the invention which is useful to yield the semiconductors AgInS₂ and AgInS₃ via pyrolysis.

FIG. 2 shows TGA profiles for [{P(n-Bu)₃, Cu(SEt)₂, In(SeEt)₂}], SSP 7 from Table 1 herein.

FIG. 3 shows the results of low temperature DSC for [{P(Bu’₃)₃, Cu(SEt)₂, In(SeEt)₂} and [{P(Bu’₃)₃, Cu(S(Pr)₃)₂, In(SPPr)₃}], SSPS according to the invention (SSPs 7 and 8 from Table 1 herein), which are liquid at room temperature.

FIG. 4a is a schematic diagram of a horizontal hot wall spray CVD reactor for the deposition of ternary SSPs according to the invention.
FIG. 46 is a schematic diagram of a vertical cold wall spray CVD reactor for the deposition of ternary SSPs according to the invention.

FIG. 5 shows an X-ray powder diffraction pattern of a CuInS$_2$ thin film deposited on molybdenum foil using the liquid SSP $\{[\text{PBu}_3]_2\text{Cu(SEt)}_2\text{In(SEt)}_2]\$ according to the invention.

FIG. 6 shows SEM micrographs of a deposited CuInS$_2$ thin film using the SSP $\{[\text{PPPh}_3]_2\text{Cu(SEt)}_2\text{In(SEt)}_2]\$ (SSP 1 from Table 1 herein).

FIG. 7 shows a current density vs. voltage plot of a Schottky barrier made from evaporated Al on CuInS$_2$ on Mo foil using the SSP $\{[\text{PBu}_3]_2\text{Cu(SEt)}_2\text{In(SEt)}_2]\$ (SSP 1 from Table 1 herein).

FIG. 8 shows the XRD pattern of a CuInS$_2$ film grown in a cold-wall reactor at 400° C. using $\{[\text{PBu}_3]_2\text{Cu(SEt)}_2\text{In(SEt)}_2]\$; graph (a): as-grown and graph (b): after annealing at 600° C. for 10 minutes under N$_2$ flow.

FIG. 9 shows a plot of (a) $E^*$ vs. E for a CuInS$_2$ film grown from $\{[\text{PBu}_3]_2\text{Cu(SEt)}_2\text{In(SEt)}_2]\$ in a cold-wall reactor, (c) an absorption coefficient estimated from the optical transmittance data and E is a photon energy.

FIG. 10 shows an SEM micrograph of the CuInS$_2$ thin film of FIG. 9, (b) shows a SEM plane-view image of the film grown in the cold-wall reactor, and (c) shows an optical microscopic image of (b) with a low magnification.

FIG. 11 shows the EGA-FTIR spectrum for $\{[\text{P(n-Bu)}_3]_2\text{Cu(SEt)}_2\text{In(SEt)}_2]\$; SSP 7 from Table 1 herein.

FIG. 12 shows the EGA-FTIR spectrum for $\{[\text{P(n-Bu)}_3]_2\text{Cu(SPPh)}_3\text{In(SPPh)}_3]\$; SSP 8 from Table 1 herein.

FIGS. 13 and 14 show EGA-MS (EI) data for $\{[\text{P(n-Bu)}_3]_2\text{Cu(SEt)}_2\text{In(SEt)}_2]\$; SSP 7 from Table 1 herein.

FIG. 15 is an XRD powder diffraction spectrum for non-volatile residue from pyrolysis of $\{[\text{P(n-Bu)}_3]_2\text{Cu(SEt)}_2\text{In(SEt)}_2]\$; SSP 7 from Table 1 herein (Cu K$\alpha$, 1.541 Å).

FIG. 16 shows seven vials of quantum dots of the same compound in solution, each vial containing quantum dots of different size.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

As used herein, when a range such as 5–25 (or 5 to 25) is given, this means preferably at least 5 and, separately and independently, preferably not more than 25. Also as used herein, the following abbreviations used to refer to chemical structures/species have the following meanings: Ph=phenyl group; E=ethyl group; Pr=propyl group; Bu=butyl group. Throughout the following description, and in the claims, the above abbreviations can be substituted for or with their empirical formula equivalents with no change in scope or meaning; i.e. Bu is the same as $-C_4H_{9}$, Ph is the same as $-C_6H_{5}$, etc.

The invention includes a single source precursor for ternary chalcopyrite materials useful as semiconductors, for example in solar collection cells. By “single source” it is meant that a precursor molecule according to the invention provides all of the necessary components (atomic species) in the appropriate stoichiometric ratios so that upon decomposition (e.g. by pyrolysis) of the precursor, a desired ternary chalcopyrite material is formed.

In a preferred embodiment, the single source precursors (SSP) of the present invention yield a ternary chalcopyrite material of the form I-III-VI$_2$, where roman numeral I refers to Group I-B from the periodic table, roman numeral III refers to Group III-A and roman numeral VI refers to Group VI-A. By ternary, it is meant that the chalcopyrite materials yielded or produced from the SSPs of the present invention contain atoms from three elemental Groups of the periodic table. For example, a ternary I-III-VI$_2$ chalcopyrite material has one atom from Group I-B, one atom from Group III-A and two atoms from Group VI-A, and therefore contains atoms from three Groups of the period table, satisfying the definition of a “ternary” chalcopyrite. CuInS$_2$ is an example of such a ternary chalcopyrite that can be produced from single source precursors according to the invention as will be further described.

It should be noted that ternary chalcopyrites include materials having multiple and/or different atoms from each of three Groups from the periodic table. For example, CuInSSe is a ternary chalcopyrite because it has Cu (Group I-B), In (Group III-A), and S and Se (both from Group VI-A). In addition, molecules of the form (Cu:Ag)(In:Ga) (S:Se), having various ratios of the respectively grouped atoms are all ternary chalcopyrites (Cu and Ag both are in Group I-B, In and Ga both are in Group III-A, S and Se both are in Group VI-A). In addition, these same ternary chalcopyrites can afford the following semiconductors of stoichiometry AgIn$_5$S$_8$ and CuIn$_5$S$_8$. In the case of the CuIn$_5$S$_8$ this is prepared when the SSPs are pyrolyzed at higher temperatures, e.g. greater than 600° C. In the case of AgIn$_5$S$_8$, its fabrication is dependent on the processing conditions, such as temperature, concentration, pressure etc.

Single source precursors according to the invention are in the form of one of the following structural formulas:
Each of the above SSPs is degradable (preferably via heating or pyrolysis as known in the art) to provide a ternary I-III-VI\textsubscript{2} chalcopyrite material of the form MM'\textsubscript{x}E\textsubscript{y}. For example, in any of the above structures (a)-(h), when M' is selected to be copper (Cu), M" is selected to be indium (In) and E is selected to be sulfur (S), the resulting SSP will yield the ternary chalcopyrite CuInS\textsubscript{2} upon degradation of the SSP. In addition, structures (a) and (b) have been found to yield ternary I-III-VI\textsubscript{2} chalcopyrites of the form MM'\textsubscript{x}E\textsubscript{y}.

It has been discovered by the inventors herein that, surprisingly and unexpectedly, suitable SSPs for ternary I-III-VI\textsubscript{2} chalcopyrite materials are not limited to those structures mentioned in the background section, but that suitable SSPs can be prepared according to any of above structural formulas (a)-(h).

The SSPs according to the invention are suitable for depositing thin film ternary I-III-VI\textsubscript{2} chalcopyrite layers via a spray CVD process. In particular, the number of "tunable" sites (particularly the R sites in the above structures) within the SSP provides a wide array of possible chemical and structural formulas for the SSPs according to the invention, which can be prepared or modified having varying compositions engineered to suit specific spray CVD processes. By selective manipulation of the steric and electronic properties of the functional groups, the SSP molecule essentially can be tuned to match the properties of a desired spray CVD process, including such thermal properties as decomposition temperatures and material phase.

In the SSP according to the invention, \([L,M'(ER)\textsubscript{x}](R)\textsubscript{z}M''\) or specifically in any of the structures (a)-(h), the Lewis base(s), L, in each structure is/are selected to provide sufficient electron donation to stabilize the M' complex (which otherwise would be highly reactive and unstable) prior to solution pyrolysis of the SSP to yield the ternary chalcopyrite. The Lewis acid-base interaction is a valuable component to the overall stability of the SSP molecule, given that the ability of the Lewis base to dissociate from the cation at lower energies is pertinent to the degradation of the SSP at reduced temperatures. Hence, the Drago-Wayland approximation, can be used for ternary single source precursor design, to quantitatively estimate the strength of the Lewis acid-base interaction between the M' center and the neutral donor.

SSPs having Lewis bases of the form PPh\textsubscript{3} and selected to be copper (Cu), M" is selected to be indium (In) and E is selected to be sulfur (S), the resulting SSP will yield the ternary chalcopyrite CuInS\textsubscript{2} upon degradation of the SSP. In addition, structures (a) and (b) have been found to yield ternary I-III-VI\textsubscript{2} chalcopyrites of the form MM'\textsubscript{x}E\textsubscript{y}.

It will be understood that the above eight structural formulas for the invented SSPs can be divided into four groups of two structures each where the only difference between the two structures is the use of one versus two coordinating Lewis base groups. These groups are [(a) and (c), (b) and (d), (e) and (g)], and [(f) and (h)]. Thus the only difference between structure (a) and structure (c) is that structure (a) utilizes two Lewis base groups whereas structure (c) utilizes a single Lewis base group that is selected to have sufficient reducing power by itself to stabilize the M' metallic center.

The above eight structural formulas for the invented SSPs can also be divided into a second set of four groups of two structures each as follows: [(a) and (b)], [(c) and (d)], [(e)
and (f). In this grouping, the difference between structures (a) and (b) is understood as follows. Structure (b) was the first generic structure of a SSP for a ternary I-III-VI to be synthesized. When a SSP having structure (b) is pyrolyzed to yield M'M"E₂, all of the R groups are denatured or burned away leaving the two metallic centers M' and M", as well as two Group VI-A E atoms. During pyrolysis of the SSP, the bridging bonds, namely M'-E(R)-M" are cleaved more easily than those between terminal E atoms and M", i.e. M"-E(R). Once all the R groups and the bridging E atoms are removed, the Lewis base bound to the M' metallic center is dissociated, leaving behind M'. Thus via a redistribution mechanism M' is attracted and forms a bond to the M" metallic center having the two terminal E atoms already bonded thereto. This yields the ternary chalcopyrite, M'M"E₂. It has been discovered, surprisingly and unexpectedly, that an SSP can be prepared similarly to structure (b) except that the terminal E atoms are be replaced with Group VII-A (halogen) atoms, and that this terminal halogen-substituted structure can be pyrolyzed to yield the same M'M"E₂ ternary chalcopyrite as the SSP of structure (b). This terminal halogen-substituted structure is shown in structure (a).

Without wishing to be bound by a particular theory, it is believed that the formation of the ternary chalcopyrite M'M"E₂ is formed via a similar redistribution mechanism as described above when a SSP of structure (a) is pyrolyzed.

Due to the thermodynamically favorable formation of X₂, (which is evolved in the gaseous state) and the semiconductor M'M"E₂ through a redistribution mechanism, these are the prime products. When only one halogen X is present in the compositional formula for the SSP, then a redistribution mechanism is still believed to be probable but it now involves two molecules of the SSP, thereby obtain one halogen atom X from each of the two SSP molecules to thus afford X₂ in the gaseous state.

SSP structures (c) and (d) are structurally analogous respectively to (a) and (b), differing therefrom only based on whether one or two Lewis base groups are used to stabilize the M' center. Accordingly, structure (c) differs from structure (d) in that the terminal E atoms from structure (d) are substituted with X (halogen) atoms in structure (c).

SSP structures (c) and (f) are related in that only two Group VI-A "E" atoms are provided, but in structure (c) they are provided in the terminal position whereas in structure (f) they are provided in the bridging position. When the E atoms are provided in the terminal position (structure (e)), halogen atoms are provided in the bridging position to join the M' and M" metallic centers, through a delocalization of their charge as will be understood by a person of ordinary skill in the art. In effect, each bridging halogen X atom supplies half of its one electron density to each of the M' and M" atoms, leaving the overall charge on the halogen atom negative. When the E atoms are provided in the bridging position (structure (f)), no terminal halogen atoms need be provided. (If terminal halogens are provided, then the SSP would be of structure (a)).

SSP structures (g) and (h) are analogous respectively to structures (e) and (f) except that only one Lewis base group is provided to stabilize the M' center.

Most preferably, a SSP according to the invention has a structure of (a) or (b), less preferably of (c) or (d), less preferably (e) or (f), less preferably (g) or (h). This preferred structural hierarchy is due to experience with ease and readiness of preparation of the SSPs, and not to any perceived greater or lesser effectiveness of the SSP to yield the desired ternary I-III-VI chalcopyrite material.

In a preferred embodiment, the SSPs according to the invention are prepared by the reaction of a stabilized Cu(I) cation, with an indium(III), or gallium(III) chalcogenide anion prepared in situ by reaction of the conjugate acid of the thiol, or selenol etc. with NaOEt in...
Scheme 2: Preferred Synthesis Reaction for Preparing Ternary I-III-VI$_3$ Chalcopyrite Materials

In carrying out the above reaction (Scheme 2), the reagents are combined in the appropriate stoichiometric ratios under aerobic or anaerobic conditions. The reaction can be carried out in a batch or continuous process to yield the SSP according to the invention. Novel Scheme 2 eliminates the need to perform a cumbersome, lengthy synthetic methodology and the need to employ expensive and/or non-commodity starting reagents. In addition, the new route has been shown to be mass scaleable which is important for commercial applications. These are novel and important features of the synthesis method of Scheme 2 above, compared to other methods of synthesizing SSPs.

Scheme 2 is a preferred method for preparing SSPs according to the invention because the reaction can be carried out using commercially available reagents under readily reproducible conditions as mentioned above. For example, reacting NaSCH$_3$ with InCl$_3$ and adding CuCl and 2PPh$_3$ (all of which are commercially available or readily prepared, R=alkyl or aryl group) in a one-pot batch reaction vessel yields $[\{PR_3\}_2Cu(SMe)_2In(SMe)_2]$ which is a SSP according to the invention of structural formula (b) above.

In a further example, the above Scheme 2 reaction pathway can be carried out to prepare the known ternary SSP $[\{P(C_6H_{5})_3\}_2Cu(SEt)In(SEt)_2]$ as follows. A 500 ml 3 neck flask is charged with NaOMe (0.5 M, 346.19 mL, 173.095 mmol), and anhydrous methanol 200 mL. HSEt (10.76 g, 12.82 mL, 173.095 mmol), is added to the reaction flask via syringe and left for 5 minutes. InCl$_3$ (9.34 g, 42.218 mmol) is rapidly added, resulting in a clear solution (on some occasions small white flocculent ppt is also observed). The mixture is stirred and allowed react for 15~30 minutes. A solution, or suspension of anhydrous CuCl (4.60 g, 46.440 mmol), and PPh$_3$ (24.36 g, 92.880 mmol), in a mixture of anhydrous CH$_2$CN/CH$_2$Cl$_2$ (3:1 volume ratio), is rapidly added to Na"\[In(SEt)$_2\]", formed in situ. An important feature of this Scheme 2 is the in situ formation of the ionic complex $[\{PPh_3\}_2Cu(SMe)_2In(SMe)_2]$ as an intermediate to the final ternary chalcopyrite product. After 24 hours the reaction is concentrated, the product extracted with CH$_2$CN (200 mL) and filtered through Celite. Evaporation of the filtrate affords the SSP precursor. A similar preparative route is used for the preparation of the Ag analogues, but in the absence of light. In the case of liquid SSPs, they can be extracted using pentane.

The versatility of this synthetic pathway is illustrated by the ability to modulate the physical properties of the SSP and composition at any of the intermediate synthetic steps by adjusting the Lewis acid-base interaction ($L\rightarrow Cu$), and/or adjusting the accessibility of the lone pair of electrons on the neutral donor ligand by variation of $R$, adjusting the bond strength between the chalcogenide with either In/Ga and Cu metal centers. The preferred pathway of Scheme 2 is further characterized by the ability to prepare SSPs containing analogues of group VI-A elements, (S, Se, Te), and the ability to prepare SSPs using either indium or gallium as the Group III-A element.

SSPs of the type $[\{L\}_2M(ER)_2M'(ER)_2]$ structure (b) above have been shown to be excellent candidates for depositing ternary I-III-VI$_3$ semiconductors, which has been established as a key component for the fabrication of the next generation of photovoltaic (PV) devices. For example current solar cells based on CuInS$_2$ and CuInSe$_2$ have shown efficiencies that are comparable to single crystal PV devices. The versatility of the $[\{L\}_2M(ER)_2M'(ER)_2]$ architecture is demonstrated by the ability to manipulate its composition, thermal and solid state properties for depositing wide band gap semiconducting materials.

One of the important parameters in developing the above Scheme 2 pathway was to maintain the flexibility of synthesis to permit tailoring of the SSP as described above. Using the Scheme 2 pathway the ternary SSP $[\{PPh_3\}_2Cu(\mu-SePh)_2In(\mu-SePh)Mo$_2$]$ and a new SSP $[\{PPh_3\}_2Cu(\mu-SMe)Mo$_2$]$ were prepared in good yields with the exception that NaSePh and NaSMe were used. Further versatility of the pathway was examined for the preparation of the analogous Ag SSP to $[\{PPh_3\}_2Ag(\mu-SMe)In(\mu-SMe)]$.

Under the absence of light the Lewis based stabilized Ag(I) metal center was prepared in situ by the reaction of AgNO$_3$ with 2 equivalents of PPh$_3$ in CH$_2$CN/CH$_2$Cl$_2$ and added directly to the indium thiolate prepared in situ. After 24 hours the product was worked up as a white crystalline material. NMR and elemental analysis confirmed the product to be $[\{PPh_3\}_2Ag(\mu-SMe)In(\mu-SMe)$.]

Crystals of the $[\{PPh_3\}_2Ag(\mu-SMe)In(\mu-SMe) SSP suitable for single-crystal X-ray diffraction studies, obtained by controlled growth from a biphasic solvent system of CH$_2$Cl$_2$/hexane at room temperature overnight, led to the determination of the structure as shown in FIG. 1.

Multinuclear NMR data have demonstrated that SSPs made according to the above reaction pathway (Scheme 2) were free from any starting reagents. Thermogravimetric analyses (TGA) were performed at ambient pressure in platinum pans on samples of the synthesized SSPs, heated at a rate of 10° C/min under a dinitrogen atmosphere. Weight loss was associated with decomposition of the complexes. Calculation of the derivative maximum rate of weight loss (%/° C. listed as MRW in Table 1, shows a range from a low of 225° C. for sample 8 to a high of 325° C. for sample 5. Calculation of the precursor efficiency to afford CISiSe as the final product, based on the residual material from the TGA experiments found the samples to be within 5% (FIG. 2).

**TABLE 1**

Thermal data for ternary single source precursors prepared by reaction pathway of Scheme 2.

<table>
<thead>
<tr>
<th>Single Source Precursor</th>
<th>TGA</th>
<th>DSC</th>
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<tbody>
<tr>
<td></td>
<td>Onset</td>
<td>MRW</td>
</tr>
<tr>
<td>1 $[{PPh_3}_2Cu(SEt)_2In(SEt)_2]$</td>
<td>236</td>
<td>269</td>
</tr>
<tr>
<td>2 $[{AsPh$_3}_2Cu(SEt)_2In(SEt)_2]$</td>
<td>205</td>
<td>233</td>
</tr>
<tr>
<td>3 $[{SePh$_3}_2Cu(SEt)_2In(SEt)_2]$</td>
<td>212</td>
<td>239</td>
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<tr>
<td>4 $[{PPh_3}_2Cu(SPh$_3$)In(SPh$_3$)$_2$]</td>
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<td>254</td>
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</table>
TABLE 1-continued

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<thead>
<tr>
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<td></td>
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<td>MRW **</td>
</tr>
<tr>
<td>[P(Bu),Cu(SePh),In(SePh)]</td>
<td>261</td>
<td>325</td>
</tr>
<tr>
<td>[P(Bu),Cu(SPh),In(SPh)]</td>
<td>233</td>
<td>253</td>
</tr>
<tr>
<td>[P(Bu),Cu(Cu)(SEt),In(SEt)]</td>
<td>189</td>
<td>238</td>
</tr>
<tr>
<td>[P(Bu),Cu(SeEt),In(SEt)]</td>
<td>171</td>
<td>225</td>
</tr>
<tr>
<td>[P(Bu),Cu(SPh),In(SePh)]</td>
<td>229</td>
<td>255</td>
</tr>
<tr>
<td>[P(Bu),Cu(SMe),In(SMe)]</td>
<td>221</td>
<td>254</td>
</tr>
<tr>
<td>[P(Bu),Cu(SePh),In(SEt)]</td>
<td>229</td>
<td>272</td>
</tr>
<tr>
<td>[P(Bu),Cu(SMe),In(SEt)]</td>
<td>187</td>
<td>239</td>
</tr>
</tbody>
</table>

*not recorded;  
**Max value listed

A further example of the flexibility of the \([\{L\},M'](ER)_2,M'(ER)_2]\) architecture to direct adjustment of these precursors are SSPs 7 and 8 from Table 1, which are the first ternary single source precursors for the deposition of CuInS₂ which are in the liquid state at room temperature (T=25°C). Preferably, SSPs that are liquid phase at room temperature according to the invention have Lewis base (L) group(s) with a large or bulky steric structure, such as strait chain alkyl groups having at least three C atoms. It is believed the steric hindrance contributed by such Lewis base groups (e.g. the butyl groups in SSPs 7 and 8 above) cause or result in the molecule being in the liquid phase at room temperature. Low temperature DSC was used to investigate the liquid phase for SSPs 7 and 8. In separate studies, SSPs 7 and 8 were subjected to both quench cooling and slow controlled cooling before being heated at 10 and 5° C/min. In low temperature DSC experiments using controlled and quenched cooling, both samples 7 and 8 were found not to show an endotherm assignable to a melting phase transition thus confirming their liquid phase at ambient temperatures (FIG. 3).

Examination of the other phase transitions reveal the main exothermic events for SSPs 7 and 8 begin with extrapolated onset temperatures of 264° C. and 239° C. (from DSC experiments), which represent the decomposition of the samples. TGA profiles for \([P(Bu)_3],Cu(SeEt),In(SEt)_2]\), SSP 7 from Table 1 above, are shown in FIG. 2.

The ability of the new precursors to thermally decompose to yield single-phase CIS (CuInS₂) was investigated by powder X-ray diffraction (XRD) analysis and Energy Dispersive Spectroscopy (EDS), on the non-volatile solids from the TGA experiments of selective compounds. Furthermore, using TGA-Evolved Gas Analysis, the volatile components from the degradation of the SSPs could be analyzed via real-time FTIR and mass spectroscopy, thus providing information for the decomposition mechanism. The examination of the real time FTIR and Mass spectra confirm that the SSP decompose by cleavage of the weaker bridging bonds and the extraction of R₃S, followed by the loss of the Lewis base. (see FIGS. 11 and 12 for SSPs 7 and 8 respectively).

For example, for SSP 7 namely \([P(Bu)_3],Cu(SEt)_2,In(SEt)_2]\), Correlation with the EGA-mass spectra allowed for the assignment to the initial loss of diethyl sulfide, as supported by the library fit and from the assignment of the fragment and parent ions (m/z=90) (FIG. 13). After approximately 15 minutes mass-spec EGA shows the absence of peaks assignable to Et₂S and the occurrence of fragment ions with a mass to charge ratio (m/z) greater then 90 with an intense peak at m/z=202. These can be assigned to the successive loss of PBu₃ on the basis of its library fit of 92% and assignment of the fragment ions (FIG. 14). XRD spectra for the non-volatile material produced from the pyrolysis of SSP 7 with the JCPDS reference patterns for CuInS₂ (27-0159), confirmed it to be single-phase CuInS₂ (see FIG. 15). Examination of the EDS spectra for the same samples shows predominant emissions due to Cu, In, and S edges, with the approximate percentage atomic composition of 27, 23 and 50 for 7 and 28, 23 and 49 for 8 respectively, thus supporting the formation of CuInS₂.

In addition to SSPs 7 and 8 from Table 1, two additional SSPs for ternary chalcopyrite materials have been isolated which are in the liquid state at room temperature: \([P(Bu)_3],Cu(SePh)_2,In(SePh)_3]\) and \([P(Bu)_3],Cu(SePh)_2,In(SEt)_2]\)

Preferably, the SSPs according to the invention degrade to yield the desired I-III-VI₂ ternary chalcopyrite at a temperature less than about 500, preferably less than 480, preferably less than 460, preferably less than 440, preferably less than 420, preferably less than 400, preferably less than 380, preferably less than 360, degrees Celsius. The low degradation temperatures of the SSPs (compared to ~800° C. or greater for conventional, multi-source precursors where two or three precursors must be combined in appropriate stoichiometric ratios) make the SSPs disclosed herein well suited for spray CVD application techniques to deposit ternary chalcopyrities as mentioned above. Spray CVD has become an advancing technique where a room temperature precursor solution is ultrasonically nebulized or atomized, and is swept into hot wall reactor, (in this case a two zone hot wall reactor, the first is a “warm zone” to drive of the solvent and the second is the “hot zone” for film deposition) (FIG. 4a). The carrier-solvent (if present) is evaporated in the warm zone, and the atomized SSP is decomposed in the hot zone, where film growth occurs as in conventional CVD. As explained in the next paragraph, spray CVD techniques minimize the need for high volatility and temperature requirements for the SSP, which are essential in metal-organic chemical vapor deposition processes (MOCVD), by delivering the precursor to the furnace as an aerosol propelled by a fast-flowing carrier gas at low temperature. The latter feature of low temperature is an important benefit since volatilizing the SSP is the conventional mode of introducing the SSP into the vapor phase. However, for thermally unstable, or SSP with no, or very little vapor pressure (as in...
In a spray CVD technique, the SSP (whether liquid at T_{amb} or a solid or liquid dissolved in a suitable solvent) is atomized into tiny droplets forming a vapor mist which is deposited in the gas phase onto the substrate to be coated with the ternary chalcopyrite on degradation of the SSP. Thus, the need for the precursor(s) and associated solvent(s) to be highly volatile, and the need to deposit the precursor(s) at high temperature in order to vaporize the precursor(s) (both required for MOCVD), are eliminated. The result is that lower temperature decomposing precursors, such as the SSPs according to the invention, can be efficiently and effectively utilized to apply a uniform ternary chalcopyrite coating on a substrate surface via a low temperature spray CVD technique.

It has been found that ternary I-III-VI\textsubscript{3} chalcopyrite films applied via spray CVD using a ternary SSP according to the invention exhibit a highly oriented (112) phase. The phase of the deposited layer can be modified from (112) oriented to (204) oriented by tuning various spray CVD parameters such as temperature, film thickness, SSP concentration, carrier gas flow rate, etc., and selecting appropriate spray CVD parameters to achieve a crystallite having the desired phase orientation is within the skill level of a person having ordinary skill in the art.

A thin film study was performed using two spray CVD techniques to apply ternary chalcopyrites from a SSP according to the invention. In the first study, the SSP was atomized and aerosolized with a suitable carrier gas using a horizontal hot wall reactor (FIG. 4a) and in the second study a vertical cold wall reactor (FIG. 4b) was used. In the hot wall reactor, the aerosol was generated by a 2.5 MHz plate nebulizer, and in the cold wall reactor a 120 kHz atomizing nozzle (Sono-Tek) was used. The aerosol was delivered into each of the reactors by argon carrier gas with a typical flow rate of 4 L/min. The hot wall reactor had two heating zones, the evaporation zone 130° C. and the deposition zone 400° C.

An automated syringe pump was used to deliver the precursor solution to the vertical cold-wall reactor at a flow rate of 1.5 mL/min, and the substrate temperature was held at about 400° C. The substrate was typically either conventionally soda-lime glass, or Corning 7059, or commercial molybdenum foil, but suitable substrates are not limited to these materials.

Films of CuInS\textsubscript{2}, were deposited on polished fused silica, Kapton\textsuperscript{TM}, stainless steel, molybdenum, nickel, titanium, and polybenzobisoxazole (PBO) substrates using each spray CVD reactor. For a typical deposition in the hot wall reactor, 1.5 grams of the ternary single source precursor was dissolved in 150 mL of toluene. The solution was atomized by a 2.5 MHz nebulizer and swept into a two-zone hot-wall reactor by a carrier gas (argon) that was presaturated with the solvent. The substrate (10x76 mm), was mounted on an inclined silicon carbide coated graphite holder, which was centered in the hot-zone. The temperature of the first, warm zone (evaporation zone) was 128±1° C. and the temperature of the second, hot zone (deposition zone) was 390±1° C., with an argon carrier gas flow rate of 4 L/min. After deposition, the films were annealed at 600±1° C. for 10 minutes, unless otherwise noted. Films were then characterized by thin film spectroscopic techniques, which are within the skill level of a person having ordinary skill in the art.

Well adhering films of CuInS\textsubscript{2} were deposited on a molybdenum substrate by spray CVD at 390° C. using [[PBu\textsubscript{3}],Cu(SEt),In(SEt),] (a liquid at room temperature), which were dark blue/black, due to variation in film thickness. As deposited, the CuInS\textsubscript{2} film was highly (112) oriented (FIG. 5).

Measurements of the atomic composition of the film using Energy Dispersive Spectroscopy (EDS) were limited to Cu and In edges since the EDS emissions for sulfur and Molybdenum overlapped. SEM-EDS data on a number of regions on the thin film gave atomic percents representative of CuInS\textsubscript{2} (see Table 2 below), and no evidence of phosphorous or carbon contamination could be detected, verifying the precursor decomposed cleanly. In Table 2, Front 1 and Front 2 refer to two points on the leading edge of the film to gas flow for the deposited semiconductor, and Back refers to the trailing edge of the deposited film with respect to gas flow.

### TABLE 2

<table>
<thead>
<tr>
<th>Atomic composition of CuInS\textsubscript{2}, (CIS) thin-film deposited using [[PBu\textsubscript{3}],Cu(SEt),In(SEt),]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic % (±2%)</td>
</tr>
<tr>
<td>Front 1</td>
</tr>
<tr>
<td>Cu</td>
</tr>
<tr>
<td>In</td>
</tr>
</tbody>
</table>

SEM micrographs of the deposited CuInS\textsubscript{2} layer are provided in FIG. 6.

The electrical properties of the deposited films using [[PBu\textsubscript{3}],Cu(SEt),In(SEt),] were evaluated by current versus voltage (IV) measurements recorded for the thin films using thermally evaporated aluminum contacts (10 mm\textsuperscript{2}), to make Schottky barrier diodes. The electrical properties of deposited films using SSP 1 from Table 1 ([PBu\textsubscript{3}],Cu(SEt),In(SEt),) showed SSP 1 to make excellent Schottky barriers. Following deposition of the films, the substrate-film was annealed at 600° C. The results are provided in FIG. 7.

As seen in FIG. 7, the Schottky barriers were excellent diodes on films annealed at 600° C., with "turn on" voltages of 0.6-0.8 V, with minimal reverse bias leakage. However, many of the contacts on the as-deposited films gave large reverse bias currents and nearly ohmic responses. This behavior was indicative of degeneracy of the semiconductor due to a high carrier density resulting from native defects. The improvement in the diode behavior of the annealed films is attributed to enhanced crystallinity and reduction of defects.

The flexibility of the SSPs according to the invention in spray CVD techniques has been further demonstrated by their use in a cold wall vertical Spray CVD reactor as described above. The XRD data obtained from the film grown using [[PBu\textsubscript{3}],Cu(SEt),In(SEt),] in the cold-wall reactor revealed the typical tetragonal chalcopyrite CuInS\textsubscript{2} phase with a 112 preferred orientation. The XRD pattern for the film grown in the cold-wall reactor from [[PBu\textsubscript{3}],Cu(SEt),In(SEt),] is shown in FIG. 8(a), and revealed the typical tetragonal chalcopyrite CuInS\textsubscript{2} phase with a weak (112) preferred crystal phase orientation including minor non detrimental phase(s) with the highest intensity at 2θ=26.3° (marked by '+' ). Post-annealing at 600° C. for 10
The band gap for the film grown from the liquid precursor 
\( \left[ \left[ \text{PbS}_{1-x} \text{CuSe}_{x} \right], \text{In(Se/Te)} \right] \), derived from a plot of (eV) vs. E (FIG. 9), was found to be \(-1.46\) eV. Although annealing the film showed a shift to a higher gradient band edge (current densities), it was found to have minimal effect on the observed band gap. SEM-EDS analysis showed the CuInSe thin-film to be near stoichiometric with atomic percents for Cu, In, and S as 26, 24, and 50 (±3%), respectively (FIG. 10).

A substantial advantage to the liquid phase SSPs (e.g. SSPs 7 and 8 from Table 1 above) is that they have been found to be highly soluble in a wide range of organic solvents, including both polar and non-polar organic solvents. Such a wide range of solubility greatly enhances and simplifies the selection of appropriate solvents when used to suit a particular application or substrate. It is believed the observed solubility of the liquid phase SSPs according to the invention in both polar and non-polar organic solvents may be attributed to their ionic character and to the long non-polar alkyl chains.

By utilizing SSPs according to the invention, ternary I-III-IV chalcopyrites can be provided by a lower temperature, less costly, non-toxic and comparatively simple procedure compared to conventional multi-source techniques. The ternary I-III-IV that can be produced via pyrolysis of one of the invented SSPs, or of a mixture of at least two of the invented SSPs e.g., to yield a semiconductor of the form [(Cu:Ag:Au)(Al:In:Ga)(S:Se:Te)]. In such an SSP, it will be understood by persons of ordinary skill in the art that the ratio of Al:In:Ga and S:Se:Te can each be independently varied such that the overall stoichiometric composition of the semiconductor remains 1:1:2, (or some desirable SSPs, 1:5:8) to produce ternary chalcopyrite semiconducting materials that have tunable band gaps between the conduction and valence bands. For example, the ratios could be designed to yield a ternary chalcopyrite material having a band gap of about 1.5 eV (CuInS2), or about 2-2.4 eV (CuGaS2) (but not limited to such). In another embodiment, ternary semiconductors of the form (Cu:Ag: Au)(Al:In:Ga)(S:Se:Te), can be prepared from SSPs according to the invention where the ratios of Al:In:Ga and S:Se:Te can all be varied or tuned to provide a semiconductor having a tunable band gap, e.g. in the range of from approx 0.5-3.5 eV.

In a preferred application, the SSPs according to the invention can be used to prepare nanocrystallites of ternary I-III-IV chalcopyrite materials by first forming nanometric particulates or droplets of the SSPs and then pyrolyzing these droplets to yield the ternary chalcopyrite. Nanocrystallites, commonly referred to as quantum dots (QDs), are materials on the order of 10^{-8} m (1 nanometer) magnitude that possess properties unlike those of their analogous bulk solids. Quantum dots exhibit extraordinary optical properties that can be readily customized by changing the size and/or composition of the quantum dots. For example, by simply adjusting the size of the quantum dots, their absorption and emission spectra can be tuned to particular applications. This property of quantum dots is very unique in that a change in particle size can change the material properties. Quantum dot-based solar cells have been shown in theoretical studies to have a potential efficiency of 66% which is approximately double that of the current state-of-the-art. A key to investigating the possibility of studying and manufacturing highly efficient QD based solar cells is a reproducible synthetic process.

By the present invention, the single source precursor can be prepared as described in detail above, having the correct atomic stoichiometry “built-in.” Ternary quantum dots are then synthesized by the following preferred procedure. The ternary SSP according to the invention is dissolved in trioctylphosphine (TOP) under an inert atmosphere. This is subsequently injected into a hot stirred solution of trietylphosphine oxide, in order to facilitate controlled pyrolysis decomposition of the ternary precursor to afford the desired capped ternary quantum dots. In a preferred embodiment, the temperature of the hot stirred solution is less than about 500, preferably less than 400, degrees Celsius. Aliquots of the solution are removed during the formation of the quantum dots and are monitored via UV/VIS spectroscopy, which provides information on their magnitude. When the desired size of the quantum dots is reached, the reaction is then cooled and methanol is added to remove excess...
reagents, to afford the TOPP-capped ternary nanocrystals (M'M'E, as described above).

For example the preparation of the CuInS₂ quantum dots has been carried out as follows: [P(n-C₄H₉)₃]₂Cu(Se-C₆H₅)₂In(Se-C₆H₅)₂ (1.945 g, 2.0 mmol) was dissolved in Dioctyl phthalate (10 mL). At approximately 150°C, the precursor dissolved to form a transparent yellow solution; no further change was observed with time at this temperature. At 150°C, the precursor remains, for the most part, intact. Upon increase of the temperature to 200°C, a red powder began to precipitate within a few minutes; a reaction time of 2 h was employed to complete the precipitation and maximize the yield. After cooling to room temperature under argon, toluene (40 mL) was added to the reaction mixture to lower the viscosity of the reaction mixture and the red powder was isolated by centrifugation. The powder was consecutively washed with toluene and methanol to remove reaction byproducts and unreacted starting material and was dried under vacuum at 60°C. The washing and centrifugation steps were carried out in ambient atmosphere. The product appeared only departing from the spirit and the scope of the present invention as set forth in the appended claims.

What is claimed is:

1. A single source precursor for the deposition of ternary chalcopyrite materials, said single source precursor having a structural formula selected from the group consisting of

2. A single source precursor according to claim 1, said single source precursor being a liquid at room temperature.

3. A single source precursor according to claim 2, said single source precursor being soluble in polar organic solvents and in non-polar organic solvents.

4. A single source precursor according to claim 1, of the formula [(P(n-C₄H₉)₃)₂Cu(Se-C₆H₅)₂In(Se-C₆H₅)₂].

5. A single source precursor according to claim 1, of the formula [(P(n-C₄H₉)₃)₂Cu(Se-C₆H₅)₂In(Se-C₆H₅)].

6. A single source precursor according to claim 1, of the formula [(P(n-C₄H₉)₃)₂Cu(Se-C₆H₅)₂In(Se-C₆H₅)].

7. A single source precursor according to claim 1, of the formula [(P(n-C₄H₉)₃)₂Cu(Se-C₆H₅)₂In(Se-C₆H₅)].

8. A single source precursor according to claim 1, of the formula [(P(n-C₄H₉)₃)₂Cu(Se-C₆H₅)₂In(Se-C₆H₅)].

9. A single source precursor according to claim 1, said single source precursor being effective to yield a I-III-VI₂ ternary chalcopyrite material upon heating or pyrolysis of said single source precursor at a temperature less than about 500°C.

10. A single source precursor according to claim 1, said single source precursor being effective to yield a ternary chalcopyrite material having a band gap of about 1.5 eV between a conduction band and a valence band thereof.

11. A single source precursor according to claim 10, said ternary chalcopyrite material being CuInS₂.

12. A single source precursor according to claim 1, said single source precursor being effective to yield a ternary chalcopyrite material having a band gap of about 2 eV between a conduction band and a valence band thereof.

13. A single source precursor according to claim 12, said ternary chalcopyrite material being CuGaS₂.

14. A single source precursor according to claim 1, said single source precursor being effective to yield a ternary chalcopyrite material having a band gap of 1.5-2 eV between a conduction band and a valence band thereof, said ternary chalcopyrite material being Cu(In:Ga)(S:Se).
wherein L is a Lewis base that is coordinated to M' via a dative bond, M' is a Group I-B atom, M" is a Group III-A atom, E is a Group VI-A atom, X is a Group VII-A atom, and each R is individually selected from the group consisting of alkyl, aryl, vinyl, perfluoro alkyl, perfluoro aryl, silane, and carbamato groups.

16. A single source precursor according to claim 15, said single source precursor being effective to yield a I-III-VI, ternary chalcopyrite material upon heating or pyrolysis of said single source precursor at a temperature less than about 500 °C.

17. A single source precursor according to claim 15, said single source precursor being effective to yield a ternary chalcopyrite material having a band gap of about 1.5 eV between a conduction band and a valence band thereof.

18. A single source precursor according to claim 17, said ternary chalcopyrite material being CuInS₂.

19. A single source precursor according to claim 15, said single source precursor being effective to yield a ternary chalcopyrite material having a band gap of about 2 eV between a conduction band and a valence band thereof.

20. A single source precursor according to claim 19, said ternary chalcopyrite material being CuGaS₂.

21. A single source precursor according to claim 15, said single source precursor being effective to yield a ternary chalcopyrite material having a band gap of about 1.5-2 eV between a conduction band and a valence band thereof, said ternary chalcopyrite material being Cu(In:Ga)(S:Se)₂.

22. A single source precursor for the deposition of ternary chalcopyrite materials, said single source precursor having a structural formula selected from the group consisting of

23. A single source precursor according to claim 22, said single source precursor being effective to yield a I-III-VI, ternary chalcopyrite material upon heating or pyrolysis of said single source precursor at a temperature less than about 500 °C.

24. A single source precursor according to claim 22, said single source precursor being effective to yield a ternary chalcopyrite material having a band gap of about 1.5 eV between a conduction band and a valence band thereof.
A single source precursor for the deposition of ternary chalcopyrite materials, said single source precursor being a liquid at room temperature and being effective to yield a ternary chalcopyrite material upon heating or pyrolysis thereof.

37. A single source precursor having a structural formula selected from the group consisting of

38. A single source precursor according to claim 37, said single source precursor being effective to yield a I-III-VI$_2$ ternary chalcopyrite material upon heating or pyrolysis of said single source precursor at a temperature less than about 500$^\circ$ C.

39. A method of depositing ternary chalcopyrite materials comprising the steps of:

a) providing a first single source precursor for said ternary chalcopyrite material, said first single source precursor having the empirical formula \([\{L\},M'(ER),L-M',M''X]'\), wherein \(x\) is 1-4, \(x+y+z=4\), \(n\) is greater than or equal to 1, \(L\) is a Lewis base that is coordinated to Group 111-A atom, \(E\) is a Group VI-A atom, \(X\) is a Group VII-A element, and \(n\) is greater than or equal to 1.

b) depositing the single source precursor on a substrate using a spray CVD technique.

40. A method according to claim 39, said single source precursor having a structural formula selected from the group consisting of

41. A method according to claim 39, said single source precursor having a structural formula selected from the group consisting of

42. A method according to claim 39, said single source precursor having a structural formula selected from the group consisting of

43. A method according to claim 39, said single source precursor having a structural formula selected from the group consisting of

44. A method according to claim 39, said single source precursor having three E-R groups.

45. A method according to claim 39, comprising the steps of providing a second single source precursor, and applying said first and second single source precursors on said substrate via said spray CVD technique.

46. A method of making a single source precursor for the deposition of ternary chalcopyrite materials comprising the step of carrying out the following reaction:

\[
4M_{alk}^+ER+M'X_r+M''X_n+M''X_nL\rightarrow [\{L\},M'(ER),M''(ER)_{r/2}]
\]

wherein

\(M_{alk}\) is an alkali metal element,
\(E\) is a Group VI-A element,
\(R\) is selected from the group consisting of alkyl, aryl, vinyl, perfluoro alkyl, perfluoro aryl, silane and carbamato groups,
\(M'\) is a Group I-B element,
\(M''\) is a Group III-A element,
\(X\) is a Group VII-A element, and
\(n\) is greater than or equal to 1.

47. A method according to claim 46, wherein said single source precursor is made in a single step consisting essentially of said reaction.

48. A method according to claim 46, wherein the ionic complex \([L(,,M''(CH_2CN)_{r/2})]'\) is formed in situ as said reaction proceeds.

49. A method according to claim 46, said reaction being carried out under anaerobic conditions.
A method according to claim 46, said reaction being carried out under non-anaerobic conditions.

A method of making a quantum dot comprising the steps of:

a) providing a single source precursor for a ternary chalcopyrite material; and

b) pyrolyzing said single source precursor to yield a quantum dot made of ternary chalcopyrite material having dimensions less than 100 nanometers.

A method according to claim 51, said quantum dot made of a ternary I-III-VI₂ chalcopyrite material.

A method according to claim 51, said quantum dot made of a ternary I-III₂-VI₈ chalcopyrite material.

A method according to claim 51, said pyrolyzing step being carried out at a temperature less than about 500°C.

A method according to claim 51, said single source precursor having the empirical formula \[ \{L\}_{x}M'(ER)_{x}(X)_{y}(R)M'' \] wherein \( x = 1-4 \), \( x+y+z=4 \), \( n \) is greater than or equal to 1, \( L \) is a Lewis base that is coordinated to \( M' \) via a dative bond, \( M' \) is a Group I-B atom, \( M'' \) is a Group III-A atom, \( E \) is a Group VI-A atom, \( X \) is a Group VII-A atom, and each \( R \) is individually selected from the group consisting of alkyl, aryl, vinyl, perfluoro alkyl, perfluoro aryl, silane, and carbamato groups.

A single source precursor according to claim 1, said single source precursor being effective to yield a I-III₂-VI₈ ternary chalcopyrite material upon heating or pyrolysis of said single source precursor.

A single source precursor according to claim 29, said single source precursor being effective to yield a ternary chalcopyrite material having a band gap of 0.5–3.5 eV between a conduction band and a valence band thereof, said ternary chalcopyrite material being \((\text{Cu:Ag:Au})_{x}(\text{Al:In:Ga})_{y}(\text{S:Se:Te})_{z}\).

A single source precursor according to claim 1, said Group VI-A atom being selected from the group consisting of S, Se and Te.

A single source precursor according to claim 15, said Group VI-A atom being selected from the group consisting of S, Se and Te.
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 20:

Line 10, after “Cu(S(i-C₄H₉))” and before “,”, please insert “--”.
Line 10, after “In(S(i-C₄H₉))” and before “,”, please insert “--”.
Line 11, after “Cu(Se(i-C₄H₉))” and before “,”, please insert “--”.
Line 11, after “In(Se(i-C₄H₉))” and before “,”, please insert “--”.

Claim 22

Line 17, please delete “soup” and insert therefor “--group--”.

Claim 35

Line 5, please delete “(S:Se)” and insert therefore “(S:Se)”.

Claim 36

Line 8, please delete “alky” and insert therefor “--alkyl--”.
Line 11, after “Cu” and before “(”, please delete the space.
Line 12, after “Cu” and before “(”, please delete the space.
Line 13, after “Cu” and before “(”, please delete the space.
Line 14, after “Cu” and before “(”, please delete the space.
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Claim 43

Line 6, please delete “  ” and insert therefore

Signed and Sealed this

Twenty-fourth Day of October, 2006

JON W. DUDAS
Director of the United States Patent and Trademark Office