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# A New Facile Route for the Preparation of Single-Source Precursors for Bulk, Thin-Film, and Nanocrystallite I–III–VI Semiconductors

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We report a new simplified synthetic procedure for commercial manufacture of ternary single-source precursors (SSPs). This new synthetic process has been successfully implemented to fabricate known SSPs on bulk scale and the first liquid SSPs to the semiconductors $CuInSe_2$ and $AgIn_xS_y$. Single crystal X-ray determination reveals the first unsolvated ternary AgInS SSP. SSPs prepared via this new route have successfully been used in a spray assisted chemical vapor deposition (CVD) process to deposit polycrystalline thin films, and for preparing ternary nanocrystallites.

Although single-source precursor (SSP) for CVD processes may be highly efficient for their intended application, their use has historically been limited to the lab and their full potential never exploited. This is primarily due to the cumbersome, or lengthy, synthetic methodology and the need to employ expensive and/or noncommodity starting reagents. Thus, a key point in designing a new CVD precursor for commercialization is one that avoids these pitfalls. Our team of NASA Glenn Research Center and external collaborators has been actively involved for the past decade on binary and polyatomic precursors for the fabrication of thin-film semiconducting layers.[1] Throughout the course of the program, materials of the type $[\{L\}_xM^{(I)}(\mu\text{-}ER)_2M^{(III)}(ER)_2]$ (L = Lewis base, M = transition/main group metal, E = group VI element, and R= organic moiety) have been developed.[1,2] We have further developed and successfully shown SSPs based on this architecture to be excellent candidates for depositing $I-III-VI_2$ type semiconductors,[3-7] which have been established as key materials for the fabrication of the next generation photovoltaic (PV) devices. For example, current solar cells based on $CuInS_2$ and $Cu(Ga:In)Se_2$ have demonstrated efficiencies of 12.5% and 18.8%, respectively.[8,9] Furthermore, the importance of ternary SSPs is exemplified by a renewed interest by groups designing SSPs to ternary chalcogenide semiconductors.[10,11]

The current *US Photovoltaic Roadmap* indicates the importance of developing new commercial processes for polycrystalline thin-film solar cells.[12] Current methods for the synthesis of $[\{L\}_xM^{(I)}(\mu\text{-}ER)_2M^{(III)}(ER)_2]$ SSPs can be lengthy and require the use of nonbulk commodity starting materials.[1,2] In attempting to make these SSPs commercially viable candidates for large-scale thin-film processes, we have devised a new simple synthetic route that employs commercially available reagents while retaining the flexibility for molecular engineering.

The SSPs are prepared by a "one-pot" type reaction as illustrated in Scheme 1. Initial investigations were conducted for the preparation of the known SSP $[\{PPh_3\}_2Cu(\mu\text{-}SEt)_2In(SEt)_2]$,[2] to the semiconductor $CuInS_2$. Under anaerobic

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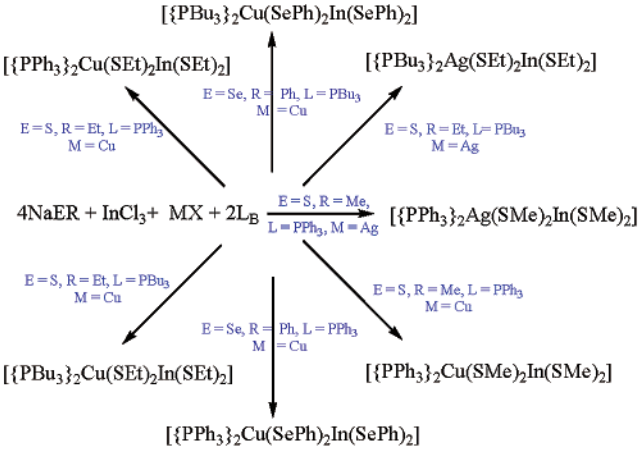
**Scheme 1.** New Preparative Route to Ternary I−III−VI SSPs



conditions, $InCl_3$ is reacted with sodium ethanethiolate in methanol in a 1:4 ratio to afford the ionic stable intermediate $Na^+[In(SEt)_4]^-$. After approximately 15 min, a solution of CuCl and the Lewis base in $CH_3CN/CH_2Cl_2$ is added directly to the freshly prepared $Na^+[In(SEt)_4]^-$. After 24 h, the reaction is essentially complete. Concentration of the methanolic solution and extraction of the product with $CH_2Cl_2$, followed by washing with dry ether and pentane, affords a creamy white solid. NMR and elemental analysis confirmed the product to be $[\{PPh_3\}_2Cu(\mu\text{-}SEt)_2In(SEt)_2]$, **1**. The flexibility of the new synthetic procedure to permit tailoring of the SSPs was also examined. Using a similar synthetic procedure to that outlined here, the ternary SSPs **2** (L = $PPh_3$, E = Se, R = Ph) and **3** (L = $PBu_3$, E = S, R = Et) and the new SSPs **4** (L= $PPh_3$, E = S, R = Me) and **5** (L = $PBu_3$, E = Se, R = Ph) were also prepared in good yields (>85%). The versatility of the route was further examined by preparing two new analogous silver ternary SSPs **6**, $[\{PPh_3\}_2Ag(\mu\text{-}SMe)_2In(SMe)_2]$, and **7**, $[\{PBu_3\}_2Ag(\mu\text{-}SEt)_2In(SEt)_2]$. After 24 h, the products are extracted as crystalline materials from $CH_2Cl_2$, or in the cases of **3** and **5** as yellow and **7** as clear liquids from pentane. Thus, SSPs **5** and **7** represent the first liquid precursors to polycrystalline $AgIn_xS_y$ and $CuInSe_2$ type semiconductors. Spectroscopic, thermal, and elemental analyses confirm the formation and purity of the products (see Supporting Information).

The key to the new preparative route is that the $M^+$ cations are very effectively solvated by MeCN, due to the high formation constants of M−NR type complexes.[13] This facilitates the formation of the desired stable tetrahedral intermediate $[M(CH_3CN)_4]^+X$ *in situ*. With the successive addition of the chosen Lewis base, the first "half" of the molecule, $[\{L\}_xM(CH_3CN)_{4-x}]^+X$, is constructed with ease and, importantly, without the need for detailed Schlenk techniques. Through experimental studies, SSPs have been prepared in yields >85% on 40 mmol scale (>30 g), thus making the procedure very attractive for mass production. Crystals of SSP **6** suitable for single crystal X-ray diffraction studies, obtained by controlled growth from a biphasic solvent system of $CH_2Cl_2$/hexane at room temperature overnight, led to the determination of its crystal structure, Figure 1.

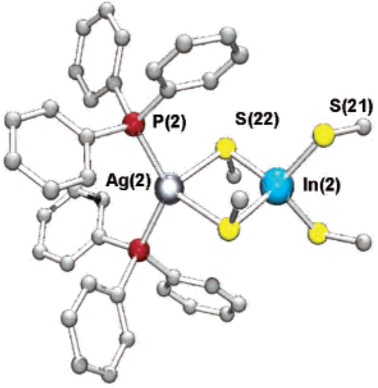


**Figure 1.** Single crystal X-ray *Pluto* representation of SSP **6**.[14] Selected bond distances (Å) and angles (deg): Ag(2)−P(2) 2.4527(10), Ag(2)−S(22) 2.6797(10), In(2)−S(21) 2.4333(11), In(2)−S(22) 2.4841(11), P(2)−Ag(2)−P(2) 128.40(5), P(2)−Ag(2)−S(22) 112.32(3), S(22)−Ag(2)−S(22) 91.03(5), In(2)−S(22)−Ag(2) 84.16(3), S(21)−In(2)−S(21) 108.91(5).

The structure is tetrahedral with respect to both the silver and indium metal centers, which are connected via two bridging methylthiolato groups, and is unique since it is the first representation of an unsolvated ternary $AgIn_xS_y$ structure of this type. Examination of the bond lengths and angles shows that they are generally unexceptional. The Ag−P distance (2.453 Å) is representative of the sum of the single bond covalent radii (2.44 Å). The P−Ag−P angle is known to vary considerably (e.g., 113−138.26°), depending on the steric and electronic properties of peripheral groups.[15] This is clearly evident, since the P−Ag−P angle of 128.41° is greater than that of 122.44° reported by Vittal and O'Brien,[11] where they report a $CHCl_3$ solvated structure with the sterically more demanding benzylthiocarboxylate group. Furthermore, the limited steric encumbrance of the −SMe group to the thiocarboxylate ligand is reflected in the smaller bond angles and length of the AgSInS cubane.

To demonstrate the utility of these advanced materials for fabricating I−III−VI semiconductors, thin films were grown in a spray CVD process. Films were frequently grown either at 760 or 30 mmHg. The thickness of a typical film ranged from 0.75 to 1.0 $\mu$m, with grain size of approximately 0.5 $\mu$m. A more in-depth study of film morphology and deposition is addressed elsewhere.[7]

Optical (Figure 2) and X-ray spectroscopic studies of the thin films deposited using the SSP synthesized via the new route were performed. Using SSP **3**, thin $CuInS_2$ films deposited at (400 °C/30 mmHg) afforded near 1:1:2 stoichometry, which were 112 orientated (see Supporting Information). Rapid thermal annealing (10 min/600 °C) was found to greatly improve the crystalline quality of the $CuInS_2$ phase, and not adversely affect the band gap.

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(14) Crystallographic data follow: space group = *P*2/*c* (No. 13), $a$ = 15.6671(4) Å, $b$ = 12.6092(4) Å, $c$ = 21.6432(8) Å, $\beta$ = 108.412(2)°, $V$ = 4056.7(4) Å$^3$, $d_{calcd}$, g cm$^{-3}$ = 1.532, $R(F_o)$ = 0.039, $R_w(F_o^2)$ = 0.076. CCDC No. 215097.

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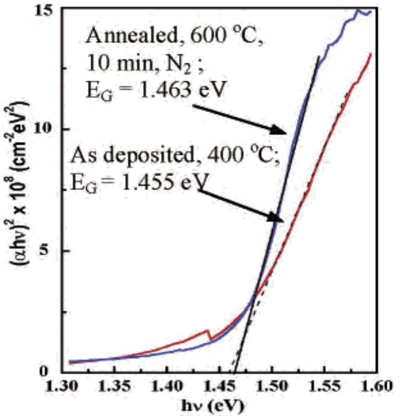

**Figure 2.** Band gap determination for $CuInS_2$ films using SSP **3**.[16]

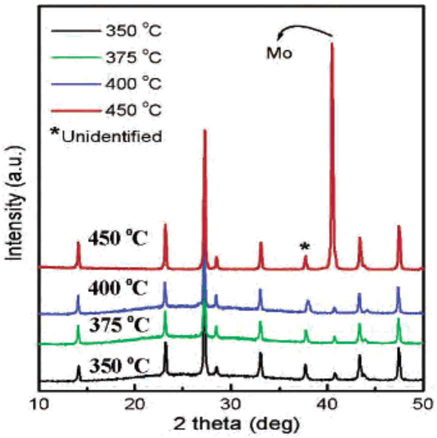

**Figure 3.** XRD spectra for as-grown $AgIn_5S_8$ films on glass and Mo/Glass, at reduced pressure (30 mmHg).

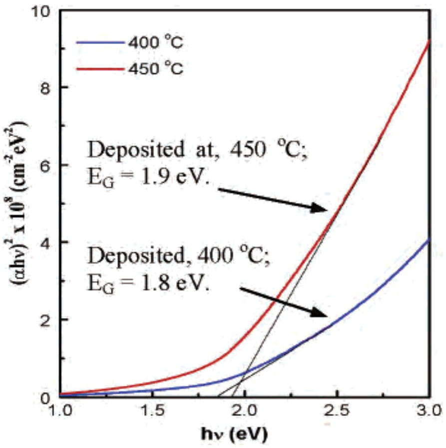

**Figure 4.** Band gap determination for as-grown $AgIn_5S_8$ thin films ($E_g$ = 1.8−1.9) (30 mmHg, liquid SSP **12**).[16]

Interestingly, X-ray diffraction (XRD) (Cu Kα, 1.541 Å), and optical characterization, of thin films grown using the new liquid AgInS SSP **7** revealed that thin films of $AgIn_5S_8$ were deposited (Figures 3 and 4), even though calculation of the atomic molar residue from TGA and XRD experiments indicated pyrolysis of **7** to afford bulk $AgInS_2$. A recent CVD study by O'Brien and Vittal using a similar SSP also showed the formation of $AgIn_5S_8$ films.[11] In order to determine whether growth temperature was responsible for the change in stoichiometry, AgInS films were deposited at a range of temperatures from 350 to 450 °C. In each case, crystalline $AgIn_5S_8$ thin films were obtained, thus indicating that substrate temperature was not a limiting factor. Further studies are underway to determine the equilibrium between $AgIn_5S_8$ and $AgInS_2$ thin film formation.

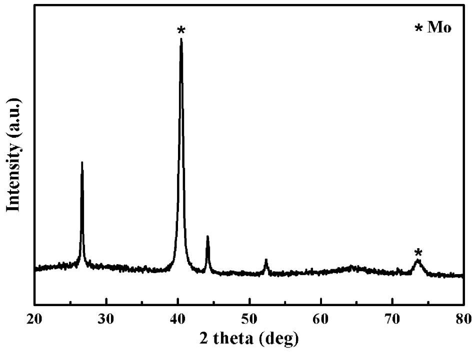

**Figure 5.** XRD of $CuInSe_2$ thin film on Mo/Glass 400 °C/30 mmHg.

In preliminary CVD studies using liquid SSP **4** to the semiconductor $CuInSe_2$, amorphous thin films could be fabricated. Films deposited at 400 °C/30 mmHg on Mo/Glass and glass showed they were 112 orientated and had near 1:1:2 stoichiometry, Figure 5. SSPs **1** and **2** prepared via the new route were also used to successfully prepare ternary nanocrystallites of $CuInS_2$ and $CuInSe_2$. A detailed and complete study has been recently published.[17]

To summarize, the versatility of the new synthetic route for the preparation of known and new SSPs to multiternary semiconductors ($[\{LR_3\}_2M(\mu\text{-}ER')_2M(ER')_2]$) is clearly demonstrated. This new synthetic route permits a simplified and easy method for fabricating SSPs without the need for noncommodity chemicals, or a detailed synthetic preparation. The new route retains flexibility, allowing full molecular engineering of the composition, stoichiometry, and solid state phase. This is shown by the preparation of the first liquid AgInS and $CuInSe_2$ SSPs, and the crystal structure determination of a unique unsolvated $[\{PPh_3\}_2Ag(\mu\text{-}SMe)_2In(SMe)_2]$ complex. SSPs made via this new route have been successfully used to prepare ternary I−III−VI bulk materials, nanocrystallites, and thin films. Importantly, the use of ternary SSPs in a spray CVD process for semiconductor fabrication now establishes itself as a viable alternative to current methods of choice (coevaporation of elementals) for fabricating I−III−$VI_2$ thin films for photovoltaic devices.

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**Supporting Information Available:** Single crystal X-ray data (CIF) and selective SEM, thermal, elemental analysis, and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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