A REVIEW OF SINGLE SOURCE PRECURSORS FOR THE DEPOSITION OF TERNARY CHALCOPYRITE MATERIALS

K. K. Banger
Ohio Aerospace Institute, Brookpark, OH 44142

J. Cowen, J. Harris, R. McClarnon, D. G. Hehemann, S. A. Duraj
Cleveland State University, Cleveland, OH 44115

D. Scheiman
QSS Inc, Cleveland, OH 44135

A. F. Hepp
NASA Glenn Research Center, Cleveland, OH 44135

ABSTRACT

The development of thin-film solar cells on flexible, lightweight, space-qualified durable substrates (i.e. Kapton) provides an attractive solution to fabricating solar arrays with high specific power, (W/kg). The syntheses and thermal modulation of ternary single source precursors, based on the $[\{LR\}_2Cu(SR')_2In(SR')_2]$ architecture in good yields are described. Thermogravimetric analyses (TGA) and Low temperature Differential Scanning Caloriometry, (DSC) demonstrate that controlled manipulation of the steric and electronic properties of either the group five-donor and/or chalcogenide moiety permits directed adjustment of the thermal stability and physical properties of the precursors. TGA-Evolved Gas Analysis, confirms that single precursors decompose by the initial extrusion of the sulphide moiety, followed by the loss of the neutral donor group, (L) to release the ternary chalcopyrite matrix. X-ray diffraction studies, EDS and SEM on the non-volatile pyrolized material demonstrate that these derivatives afford single-phase $CuInS_2/CuInSe_2$ materials at low temperature. Thin-film fabrication studies demonstrate that these single source precursors can be used in a spray chemical vapor deposition process, for depositing $CuInS_2$ onto flexible polymer substrates at temperatures less than $400°C$.
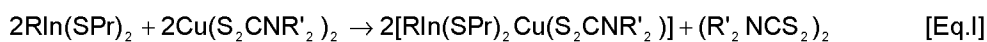
INTRODUCTION

Photovoltaic modules based on ternary chalcopyrite absorber layers, (I-III-VI$_2$; Cu(In,Ga)(S,Se)$_2$) have been the focus of intense investigation for over two decades. The use of chalcopyrite absorber are highly appealing since their bandgaps correlate well for their use in terrestrial (AM 1.5), and low orbital space applications (AM0), whilst displaying long term stability and excellent radiation tolerance [1,2]. Additionally, by adjusting the percentage atomic composition of either Ga for In and/or S for Se, the bandgap can be tuned from 1.0 eV to 2.4 eV, thus permitting fabrication of high, or graded bandgaps [3]. One of the most promising technologies lies in the development of polycrystalline thin films, since their lightweight structure enables them to achieve higher specific power (WKg^{-1}), than alternative single crystalline devices [4]. Thus, a key step of device fabrication for thin film solar cells is the deposition onto flexible, lightweight, space-qualified substrates such as polyimides.

Current methods of choice for the depositing ternary crystallite compounds, i.e. co-evaporation of elements [5-7], or binary elements [8], electrodeposition [9], reactive-sintering [10], flash evaporation [11] involve toxic sulphurization/selenization steps, often at elevated temperatures. Furthermore, under these conditions loss of volatile In/Ga chalcogenides is reported [5,12]. The requirement of high temperature deposition makes this technique incompatible with all presently known flexible polyimides, or other polymer substrates. In addition, use of toxic reagents is a limiting factor. The use of multi-source inorganic/organometallic precursors in a CVD type process is more appealing due to milder process parameters. However, stoichiometry control of deposited films can be difficult to achieve, and film contamination is evident [13], or the use of toxic pyrophoric precursors are required [14]. A novel approach is the use of ternary single source precursors, (SSP), which have the I-III-VI$_2$ stoichiometry built in and are suitable for low temperature deposition. Although, a rich and diverse array of binary SSP are known, characterized, reviewed and tested, the number of reports for the preparation of ternary SSP are limited, in addition to their use in deposition processes [15].
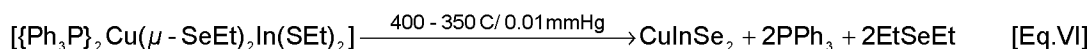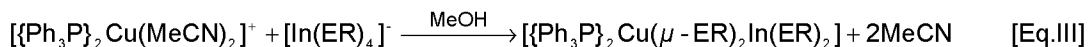
BACKGROUND

In early studies Nomura *et al*, reported that an equimolar mixture of Bu^i_2InSPr and $Cu(S_2CNBu_2)_2$ decomposed to afford $CuInS_2$ powders [16]. On this basis, solution pyrolysis of this mixture dissolved in *p*-xylene was used to deposit thin-film $CuInS_2$ at 350 °C onto glass substrates. Film composition was determined by XRD, which showed broad peaks. XRD revealed the ratios of In/Cu and S/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^i_2InSPr and $Cu(S_2CNBu_2)_2$ (as used in solution pyrolysis) afforded a single source precursor $[Bu_2In(SPr^i)Cu(S_2CNPr^i_2)]$ before decomposing to the chalcopyrite matrix [17]. Analytical and spectral data confirmed that the mixture of Bu^i_2InSPr and $Cu(S_2CNBu_2)_2$ yielded a SSP. A number of analogous ternary CIS precursors were also synthesized by the reaction of alkyl indium thiolates with copper dithiocarbamates, [Eq.I] [18]. However, only $[Bu_2In(SPr^i)Cu(S_2CNPr^i_2)]$ was successfully implemented for depositing pure $CuInS_2$ by low pressure MOCVD. . In the case of $[BuIn(SPr^i)_2Cu(S_2CNR'_2)]$, tetragonal $CuIn_5S_8$ was deposited, [Eq.II] [19].

$$2RIn(SPr)_2 + 2Cu(S_2CNR'_2)_2 \rightarrow 2[RIn(SPr)_2Cu(S_2CNR'_2)] + (R'_2NCS_2)_2 \qquad \text{[Eq.I]}$$

$$[BuIn(SPr)_2Cu(S_2CNR'_2)] \xrightarrow{\text{400 C/ 0.6 torr}} Cu_5InS_8 \qquad \text{[Eq.II]}$$

$$R = Bu, Bu^i, Bu^s; R' = Et, Bu.$$

Although the structure of these SSP were unresolved, it can be envisaged that their utility could be extended for the deposition of Ga and or Se based ternary thin-films, by using gallium thiolates/selenolates with copper dithio/diseleno carbamates. Furthermore, careful molecular design by selectively introducing S or Se groups into only one of the Ga/In, or copper reagents may aid in determining the decomposition mechanism of the precursor, in addition to serving as a $CuIn(S,Se)_2$ source, for example, $[Bu_2In(SePr^i)Cu(S_2CNPr^i_2)]$.

In early 1990 Kanatzidis *et al* reported the preparation of hetro binuclear complexes consisting of tetrahedrally arranged Cu and In centers, with two bridging thiolato and selenolato groups, [Eq.III] [20]. Pyrolysis studies undertaken revealed that the Se derivative could be converted into $CuInSe_2$ at 400-450 °C @ 0.01 mm Hg [Eq.VI], but none of the precursors had been evaluated in a thin-film deposition study.

$$[\{Ph_3P\}_2Cu(MeCN)_2]^+ + [In(ER)_4]^- \xrightarrow{\text{MeOH}} [\{Ph_3P\}_2Cu(\mu\text{-}ER)_2In(ER)_2] + 2MeCN \qquad \text{[Eq.III]}$$

$$[\{Ph_3P\}_2Cu(\mu\text{-}SeEt)_2In(SEt)_2] \xrightarrow{\text{400 - 350 C/ 0.01mmHg}} CuInSe_2 + 2PPh_3 + 2EtSeEt \qquad \text{[Eq.VI]}$$

In continuing work, Buhro and Hepp were able to demonstrate that $[\{PPh_3\}_2Cu(SEt)_2In(SEt)_2]$ could be utilized in a spray CVD process, for depositing thin-film $CuInS_2$ below 400 °C [21-22]. Thin film where deposited using a dual solvent system of toluene and dichloromethane, (CH_2Cl_2) as the carrier solvent. Single phase 112 orientated $CuInS_2$ thin films were successfully deposited at a range of temperatures from 300 to 400 °C, whilst at elevated temperatures (500 °C), $CuIn_5S_8$ phase thin films could be deposited. RBS EDS and XPS analysis showed that the films were free from any detectable impurities and highly crystalline, thus concluding the precursor decomposes cleanly. During the course of the study, the morphology of the deposited thin films where found to be temperature, and carrier solvent dependent. Films deposited at 300 °C and 350 °C yielded grain size of 400-800 nm, with smaller finer particles of 50-200 nm resident on top. At higher deposition 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 on the confirmed that deposited $CuInS_2$ thin films were direct bandgap semiconductors. In addition, the preparation of the first $CuGaS_2$ SSP, $[\{PPh_3\}_2Cu(SEt)_2Ga(SEt)_2]$ was also synthesized, although the structure was not elucidated [23]. XRD and RBS characterization of the pyrolysed material, (350-400 °C, 0.01 mmHg) and spray CVD deposited material confirmed the ternary Ga SSP to afford single phase $CuGaS_2$.

Very recent research at NASA Glenn has successfully reported the fabrication of the first ternary chalcopyrite quantum dots synthesized from ternary single source precursors, hence further extending their utility [24].

In the course of our investigations for improved single source precursors for the spray CVD of chalcopyrite thin-films, to the ternary semiconductor $Cu(Ga/In)(Se/S)_2$, we have continued to expand the molecular design of SSP based on the $[\{LR_3\}_2Cu(ER')_2In(ER')_2]$ architecture [20]. Primarily due to the limited preparation and investigation for their use in a spray CVD process. Furthermore, the number of "tunable" sites within the complex allows for their utility in preparing a number of ternary chalcopyrites of varying composition, in addition to engineer the SSP to match a given spray CVD process.

EXPERIMENTAL

All manipulations were carried out under anaerobic condition using standard Schlenk-line techniques. Multinuclear NMR, Differential Scanning Caloriometry (DSC), and Thermogravimetric analyses (TGA) with evolved gas analysis, (EGA) were used to characterize and verify precursor formation and purity. The complexes are synthesized based on modification of the procedure reported by Kanatzidis [20], with the exception of the thiolate/selenoato anion being generated *in situ* by reaction of the conjugate acid with NaOEt in methanol. The thiolate/selenoate was prepared *in situ* by reaction of NaOEt (24.25 mmol) with thiol/senenol (23.01 mmol) in anhydrous methanol.

After 30 minutes, $InCl_3$ (1.27 g, 5.75 mmol) was added affording a clear solution and the mixture was stirred for 1hr. $[Cu(CH_3CN)_2L_2]PF_6$ (5.75 mmol), dissolved in anhydrous CH_2Cl_2 (20 mL) was added dropwise to the reaction flask. The mixture was stirred (~1 to 2 d) resulting in the precipitation of a white solid. The reaction solution was then concentrated and the product extracted with anhydrous CH_2Cl_2 (50 mL,) and filtered through celite to remove the inorganic salts. The collected filtrate was concentrated via rotary evaporation. The solid precursors can then be used as is or further purified by washing with cold anhydrous diethyl ether, (3x 20 mL) and then finally anhydrous pentane, (2x10 mL). The multi-stage synthesis yields the desired products in good yields, (> 65 %) as opaque liquids, or solids with varying stability in air.
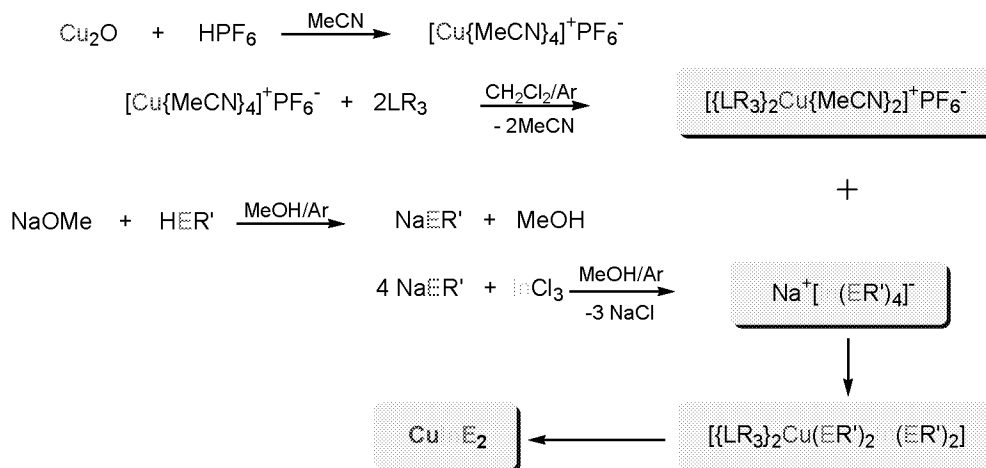
Films of $CuInS_2$ were deposited on molybdenum substrates using a spray CVD reactor similar to those described elsewhere, [23,25]. For a typical deposition, 1.5 g of the SSP was dissolved in 150 ml of toluene. The solution was atomized by a 2.5 MHz nebulizer and swept into a two-zone hot-wall reactor by a carrier gas (argon) that was pre-saturated with the solvent. The temperature of the first zone (evaporation zone) was 128 $\pm1°$C and the temperature of the second zone (deposition zone) ranged from 390$\pm1°$C. Carrier gas flow rate was 4 L/min.

Where possible deposited films were characterized by transmission spectroscopy (Perkin Elmer, Lambda-19), scanning electron microscopy (SEM) (Hitachi S-3000N), Energy Dispersive Spectroscopy (SEM-EDS) (EDAX), profileometry (KLA-Tencor HRP 75) and X-ray diffraction Philips PW3710, (Cu Kα, 1.541 Å). Reported SEM-EDS measurements are accurate to $\pm3\%$. Thermal analyses were performed on TA Instruments TGA 2950 using Platinum plans under a dinitrogen atmosphere, (ramp 10 °C/min) and TA Instruments DSC 910/MDSC 2910 under a dinitrogen atmosphere, in hermetically sealed aluminum pans.

RESULTS & DISSCUSSION

The SSP are prepared by the reaction of a stabilized Cu(I) cation, with an Indium(III) chalcogenide anion prepared *in situ* by reaction of the conjugate acid of the thiol or senenol with NaOEt in methanol. An advantage of this method is no adverse side products are produced, in addition to an "activated" thiolate/selenonate anion. During the course of the reaction the more labile MeCN ligands are displaced in preference to the thermodynamically stable chalcogenide-Cu bond formation, (Scheme I).

Scheme I. Synthesis of ternary single source precursors

$$Cu_2O \ + \ HPF_6 \ \xrightarrow{\ MeCN\ } \ [Cu\{MeCN\}_4]^+PF_6^-$$

$$[Cu\{MeCN\}_4]^+PF_6^- \ + \ 2LR_3 \ \xrightarrow[-2MeCN]{\ CH_2Cl_2/Ar\ } \ [\{LR_3\}_2Cu\{MeCN\}_2]^+PF_6^-$$

$$+$$

$$NaOMe \ + \ HER' \ \xrightarrow{\ MeOH/Ar\ } \ NaER' \ + \ MeOH$$

$$4\,NaER' \ + \ InCl_3 \ \xrightarrow[-3\,NaCl]{\ MeOH/Ar\ } \ Na^+[In(ER')_4]^-$$

$$CuInE_2 \ \longleftarrow \ [\{LR_3\}_2Cu(ER')_2In(ER')_2]$$

L = P, As, Sb; E = S, Se; R' & R = alkyl, aryl

The versatility of this synthetic pathway can be illustrated by ability to modulate the physical properties of the precursor and composition at any of the intermediate synthetic steps by either;

- Adjusting the Lewis acid-base interaction (L→Cu)
- 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 ability to prepare analogues of group 16, (S, Se, Te)
- The ability to prepare either indium or gallium derivatives

The Lewis acid-base interaction is a valuable component to the overall stability of the molecule, given that the ability of the Lewis base to dissociate from the cation at lower energies is pertinent to the degradation of the precursor at reduced temperatures. Hence, the Drago-Wayland approximation, [26] can be used for ternary single source precursor design, to quantitatively estimate the strength of the Lewis acid-base interaction between the copper center and the neutral donor. The cleavage of chalcogenide-R' bond also plays an important role, since this allows the chalcogenide to be released for incorporation into the ternary chalcopyrite matrix. Hence, the use of a sterically demanding R' group of good "leaving ability", would promote the facile release of the chalcogenide.

Initial studies focused on basic modification of the SSP, and their influence on precursor stability. Multinuclear NMR data demonstrated that the precursors were free from any starting reagents. Thermogravimetric analyses (TGA) were performed at ambient pressure in platinum pans on samples of the precursors, 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 I, shows a range from a low of 225 °C for **8** to a high of 325 °C for **5**. Calculation of the precursor efficiency to afford CIS/Se as the final product, based on the residual material from the TGA experiments found the samples to be within 5 % (Figure Ia).

Table I. Thermal data for ternary Single Source precursors.

Single Source Precursors	TGA			DSC	
	Extrap. Onset $^\circ$C	MRW $^\circ$C / %	Residue %	M.P. $^\circ$C	Decomp. $^\circ$C
1 [{PPh$_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$]	236	269	25	122	266
2 [{AsPh$_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$]	205	233	18	47	276
3 [{SbPh$_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$]	212	239	26	45	271
4 [{PPh$_3$}$_2$Cu(SPr^i)$_2$In(SPr^i)$_2$]	215	254	29	163	260
5 [{PPh$_3$}$_2$Cu(SPh)$_2$In(SPh)$_2$]	261	325	22	117	280
6 [{PPh$_3$}$_2$Cu(SePh)$_2$In(SePh)$_2$]	223	253	22	53	219
7 [{P(Bu^n)$_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$]	189	238	31	-	264
8 [{P(Bu^n)$_3$}$_2$Cu(S(Pr^n))$_2$In(SPr^n)$_2$]	171	225	29	-	239

Preliminary Vacuum-TGA studies for the "smoothed" profile for the SSP **7**, shows the extrapolated onset can be lowered by approx 80 $^\circ$C thus lowering the degradation temperature window and making these precursors model candidates for use in low temperature/pressure spray CVD on space qualified substrates such as Kapton™ (Figure Ib).
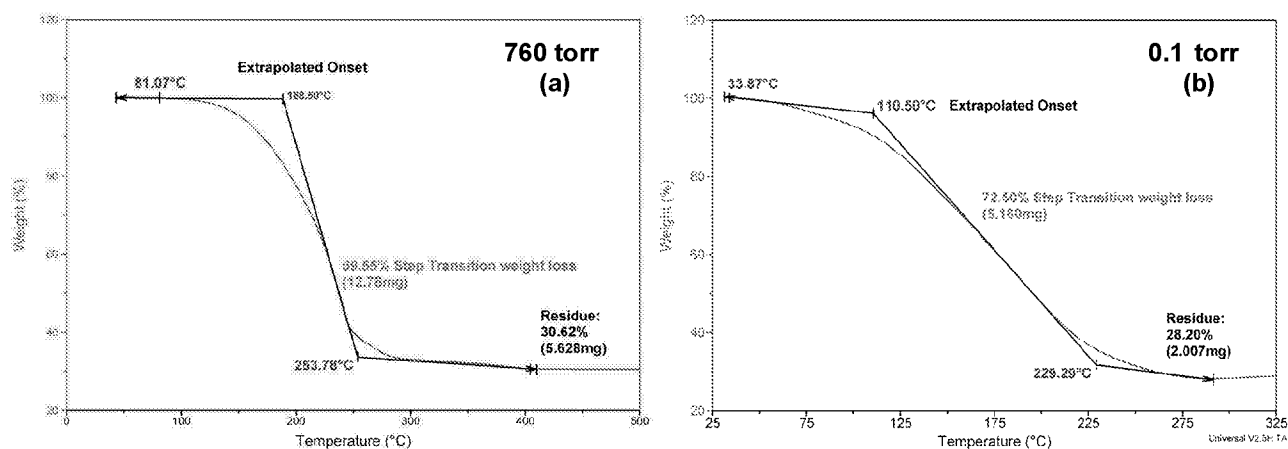

Figure I. TGA profiles for [{P(n-Bu)$_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$], **7**.

A further example of the flexibility of the [{ER$_3$}$_2$Cu(YR')$_2$In(YR')$_2$] architecture to direct adjustment of these precursors are the SSP **7** and **8**, which have a liquid solid-state phase. Low temperature DSC was used to investigate the liquid phase for **7** and **8**. In separate studies, samples **7** and **8** were subjected to both quench cooling and slow controlled cooling before being heated at 10 $^\circ$C/min and 5 $^\circ$C/min. The higher heating rates were chosen since this is preferable to enhance resolution for the observation of a finite onset point assignable to melting [27]. In low temperature DSC experiments using controlled cooling, both samples **7** and **8** were found not to show an endotherm assignable to a melting phase transition (Figure II).
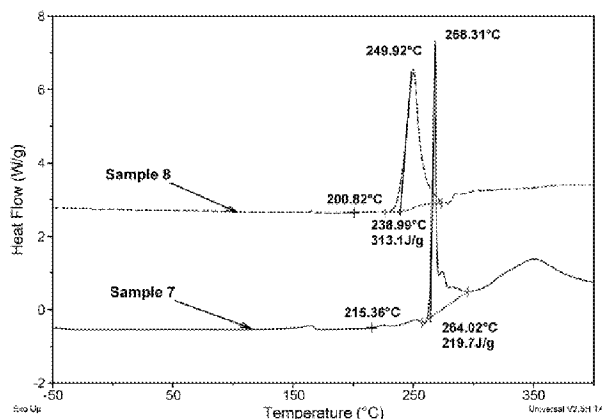
Figure II. Low temperature DSC for $[\{P(Bu^n)_3\}_2Cu(SEt)_2In(SEt)_2]$ **7** and $[\{P(Bu^n)_3\}_2Cu(S(Pr^n))_2In(SPr^n)_2]$ **8**.

In similar quench cooling experiments, an endothermic phase change assignable to a melt was also not observed. Although Modulated-DSC is known to provide greater sensitivity to deconvolute small phase transitions, studies using this technique also demonstrated the absence of an endothermic phase transition assignable to a melt. This may be attributed to the fact that MDSC uses a sinusoidal heat flow, hence the "resident time" during control cooling may not be sufficient to allow the material to undergo cold crystallization. Therefore, under these various test conditions it can be validated that sample **7** and **8** have a liquid phase at ambient temperatures. Examination of the other phase transitions reveal the main exothermic events for **7** and **8** begin with extrapolated onset temperatures of 264 °C and 239 °C, which can be assigned to the decomposition of the samples. The lower decomposition temperature of **8** can be explained, since an increase in chain length and/or steric "bulk" of the alkyl groups is known to decrease the stability of a complex [15].

Thermal analysis experiments demonstrate that the physical and chemical properties of these complexes are easily controlled by directed adjustment on one, or more of the "tunable" sites within the complex. Analysis of the thermal data shows that precursors stability can be modified by even minor adjustment of either the electronic or steric effects of the peripheral groups of the precursors. A more detailed interpretation of how the thermal properties of these materials can be modulated is presented elsewhere [28]. To verify the mechanism of decomposition for the precursors, TGA-Evolved Gas Analysis via FTIR and mass spectrometry was investigated. The real time FTIR spectrum for 7 and 8 shows absorptions at approx 3000, 1460, 1390, 1300 and 1250 cm^{-1} (Figure III).
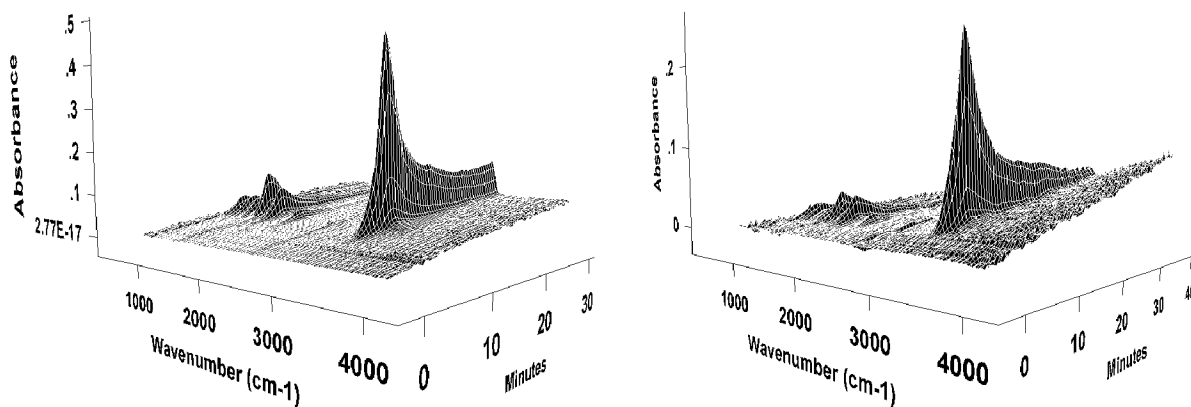

Figure III. EGA-FTIR spectra for $[\{P(n\text{-}Bu)_3\}_2Cu(SEt)_2In(SEt)_2]$ **7** and $[\{P(n\text{-}Bu)_3\}_2Cu(SPr)_2In(SPr)_2]$, **8**.

Correlation with the EGA-mass spectra allows for the assignment to the initial loss of diethyl sulphide, as supported by the library fit and from the assignment of the fragment and parent ions (m/z = 90) (Figure IVa). After approximately 15 minutes mass-spec EGA shows the absence of peaks assignable to Et_2S 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 PBu_3 on the basis of its library fit of 92 % and assignment of the fragment ions (Figure IVb). In similar experiments, EGA for the *n*-propyl derivative **8** gave analogous results, however for samples **1-6**, EGA was only able to confirm the extrusion of the dialkyl/diaryl sulphide moiety. The inability to detect the neutral group V donors may be attributed to their lower volatility.
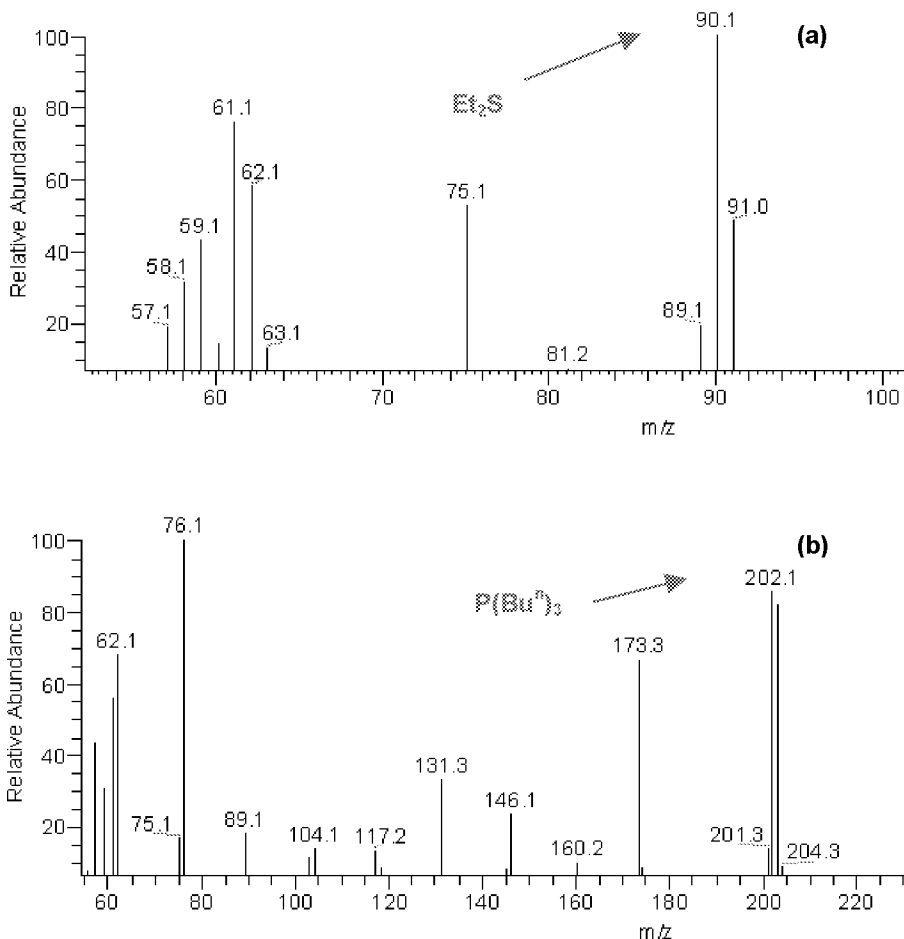

Figure IV. EGA: Mass Spec data from TGA for [{P(*n*-Bu)$_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$], **7**.

Thus, the use of TGA-EGA provides conclusive evidence for the mechanism of decomposition for the single source precursors to occur via the loss of a sulphide moiety, followed by loss of the neutral donor ligand.

The ability of the new precursor to thermally decompose to yield single-phase CIS 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. XRD spectra for the non-volatile material produced from the pyrolysis of **7** with the JCPDS reference patterns for $CuInS_2$ (27-0159), confirmed it to be single-phase $CuInS_2$ (Figure V).
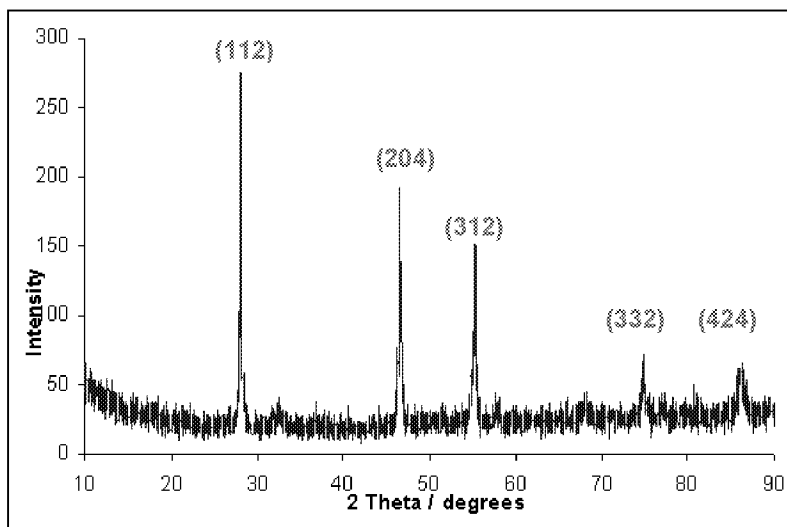
Figure V. XRD Powder Diffraction for non-volatile residue from pyrolysis of [{P(n-Bu)$_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$], (Cu Kα, 1.541 Å).

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 CuInS$_2$. SEM images of the non-volatile residue (CuInS$_2$) from the TGA experiments for sample **7** and **8** show grain size of ~1μm (Figure VI).
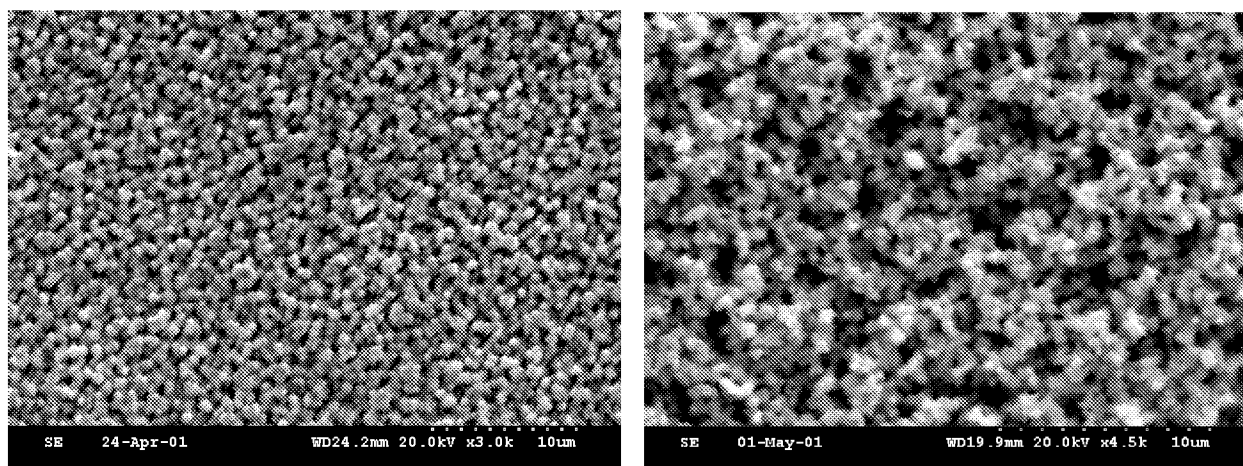

Figure VI. SEM of non-volatile residue from TGA for [{P(n-Bu)$_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$], **7**, Grain size ~ 1 μm; [{P(n-Bu)$_3$}$_2$Cu(SPr^n)$_2$In(SPr^n)$_2$], **8**.

The suitability of some of these single source precursors for the fabrication of thin-film CIS absorber has been investigated, and these results are reported in detail elsewhere [25,29]. Herein we report the first studies in the attempt to use the liquid precursor in a Spray CVD process. Well adhering films of CuInS$_2$ were deposited on a Molybdenum substrate by spray CVD at 390°C using [{PBu$_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$], which were dark blue/black, due to variation in film thickness. Unfortunately due to the limited quantities of liquid precursor for thin-film deposition studies, film thickness was too low to obtain an adequate SEM image. However, XRD and EDS data were recorded.

As deposited, the majority of CuInS$_2$ film is highly (112) oriented (Figure. VII), which is ideal since the preferred orientation for CIS films used in photovoltaic devices is (112) as these films have a low series resistance [30].
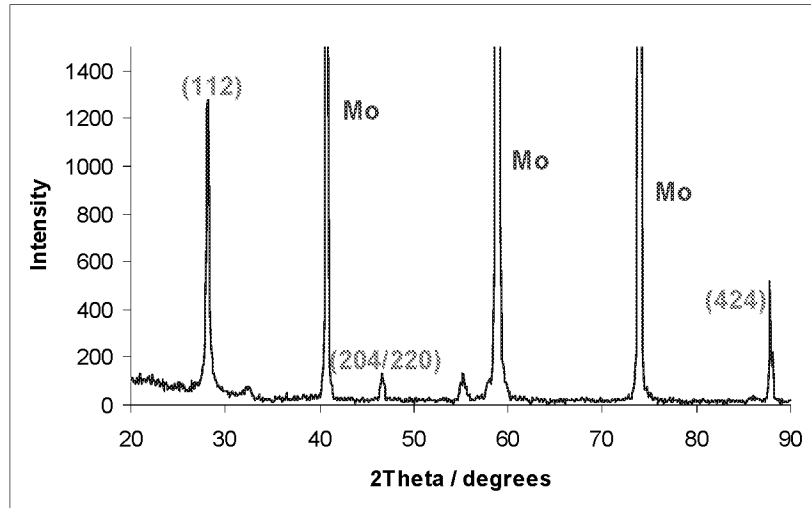

Figure VII. X-ray powder diffraction spectra of a CuInS$_2$ film on Mo (back half of the substrate).

Since the EDS emissions for sulfur and Molybdenum overlap, measurements were limited to recording emissions for only the Cu and In edges. SEM-EDS data on a number of regions on the thin film gave atomic percents representative of CuInS$_2$ (Table II), in addition, no evidence of phosphorous or carbon contamination could be detected, verifying that the precursor decomposes cleanly as evidenced in EGA-TGA studies.

Table II. Atomic composition of CIS thin-film deposited using SSP **7**.

	Atomic %, (± 3 %)		
	Front 1	`Front 2	Back
Cu	50	51	50
In	50	49	50

No electronic properties of the film could be preformed since film thickness was insufficient for device fabrication. However, the electrical properties of deposited films using SSP **1** were suitable for current verses voltage (IV) measurements to be recorded using thermally evaporated aluminum to make Schottky barriers. Many of the Schottky barriers exhibited excellent diode behavior (Figure VIII), furthermore, rapid thermal annealing of the films at 600°C for five minutes, more then doubled the current density of the diodes at 0.9 Volts and improved the reverse bias leakage. The improvement in the diode behavior is attributed to enhanced crystallinity and reduction of defects in the annealed films, as considerable narrowing of the diffraction lines was observed in the annealed films. Unfortunately, the higher annealing temperature is not compatible with deposition onto space qualified polymer substrates. It is hoped that by use of more labile single source precursors, improved electrical properties can be achieved without annealing.
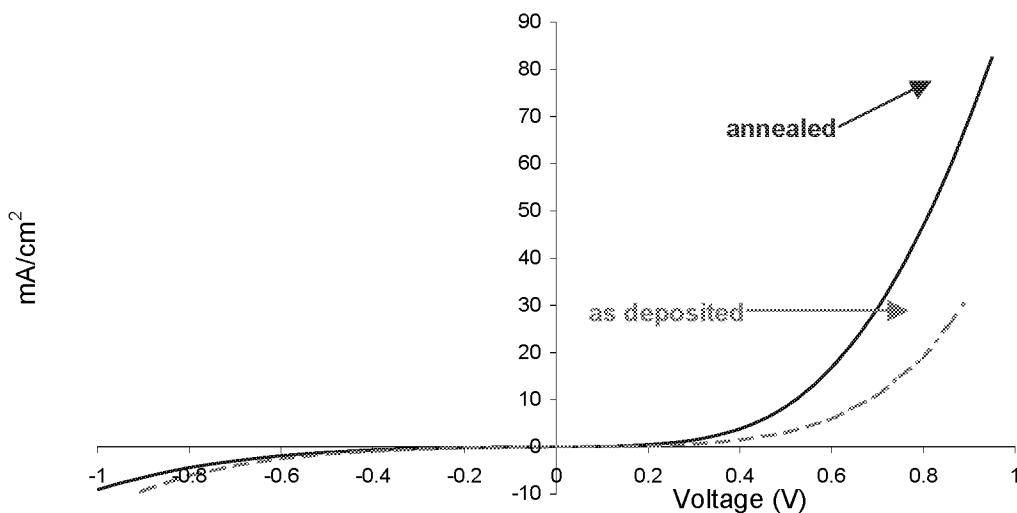
Figure VIII. Current density vs. voltage plot of Schottky barrier made from evaporated Al on $CuInS_2$ on Mo foil for both as-deposited and annealed films using SSP **1**, (Al contacts ~ 0.04 mm^2)

SUMMARY

Thermal analysis data substantiates that even minor adjustment of the steric and electronic properties on either the neutral donor, or chalcogenide groups, permits adjustment of the solid-state phase and stability of the precursor. Evolved gas analysis via mass-spec FTIR spectroscopy, confirms the mechanism of decomposition for the SSP proceeds by the loss of the sulphide group, followed by loss of the neutral donor. XRD and EDS show that the non-volatile materials from pyrolysis studies afford single-phase $CuInS_2$ and $CuInSe_2$. Thin-film fabrication studies successfully demonstrate that by using a single source organometallic precursor in conjunction with spray chemical vapor deposition, $CuInS_2$ can be deposited on flexible polymer substrates at temperatures less than $400°C$.

REFERENCES

[1] S. G. Bailey, D. J. Flood, "Space photovoltaics", Prog. Photovoltaics Res. Appl., **6**, p.1, 1998. ; (b) H. W. Schock, R. Noufi, "CIGS-based solar cells for the next Millennium", Prog. Photovolt. Res. Appl., **8**, 151-160

[2] H. W. Schock, K. Bogus, "Development of CIS solar cells for space applications", Proc. 2nd World Conf. On Photovolt. Energy Conf., Eds. J. Schmid, H. A. Ossenbrink, P. Helm, H. Ehmann and E. D. Dunlop, 3586, E. C. Joint Res. Center, Luxembourg, 1998.

[3] D. Tarrant, J. Ermer, I-III-VI_2 multinary solar cells based on $CuInSe_2$, Proceedings 23rd IEEE Photovoltaic Specialist Conference, Louisville, KY, IEEE, New York, pp. 372, 1993.

[4] D. Hoffman, T. Kerslake, A. Hepp, R. Raffaelle, "Thin-Film Solar Array Earth-Orbit Mission Applicability Assessment", XVII Space Photovoltaic Research and Tech. Conf., 2001.

[5] B. M. Basol, V. K. Kapur, A. Halani, C. Leidholm, J. Sharp, J. R. Sites, A. Swartzlander, R. Matson, H. Ullal, "Cu(In,Ga)Se_2 thin films and solar cells prepared by selenization of metallic precursors", Journal of Vacuum Science and Technology A, **14A**, p. 2251, 1996.

[6]   V. Probst, W. Stetter, W. Riedl, H. Vogt, M. Wendl, H. Calwer, S. Zweigart, K. Ufert, B. Freienstein, H. Cerva, F. H. Karg, "Rapid CIS-process for high efficiency PV-Modules: development towards large area processing", Thin Solid Films, **387**, p. 262, 2001.

[7]   B. Dimmler, H. W. Schock, "Scalability and pilot operation in solar cells of $CuInSe_2$ and their alloys", Prog. Photovolt. Res. Appl., **6**, p. 193, 1998.

[8]   S. C. Park, D. Y. Lee, B. T. Ahn, K. H. Yoon, J. Song, "Fabrication of $CuInSe_2$ films and solar cells by sequential evaporation of In_2Se_3 and Cu_2Se binary compounds", Sol. Energy Mater. Sol. Cells, **69**, p. 99, 2001.

[9]   C. Guillen, J. Herrero, "Recrystallization and components redistribution processes in electrodeposited $CuInSe_2$ thin films", Thin Solid Films, **387**, p.57, 2001

[10] C. Eberspacher, C. Fredric, K. Pauls, J. Serra, "Thin-film CIS alloy PV materials fabricated using non-vacuum, particles-based techniques", Thin Solid Films, **387**, p.18, 2001.

[11] M. Klenk, O. Schenker, V. Alberts, E. Bucher, "Properties of flash evaporated chalcopyrite absorber films and solar cells", Thin solid Films, **387**, p. 47, 2001.

[12] C. Dzionk, H. Metzner, S. Hessler, H. E. Mahnke, " Phase formation during the reactive annealing of Cu-In films in H_2S atmosphere". Thin Solid Films, **299**, p. 38, 1997.

[13] M. Krunks, V. Mikli, O. Bijakina, H. Rebane, A. Mere, T. Varema, E. Mellikov, "Composition and structure of $CuInS_2$ films prepared by spray pyrolysis", Thin Solid Films, **361-362**, p.61, 2000.

[14] M. C. Artaud, F. Ouchen, L. Martin, S. Duchemin, "$CuInSe_2$ thin films grown by MOCVD: characterization, first devices", Thin Solid Films, **324**, p. 115, 1998.

[15] A. C. Jones, P. O'Brien, "CVD of Compound Semiconductors: Precursors Synthesis, Development & Application", VCH Press, 1997.

[16] R. Nomura, K. Kanaya, H. Matsuda, "Preparation of Copper-Indium-Sulfide thin films by solution Pyrolysis of organometallic sources", Chem. Let., p. 1849, 1988.

[17] R. Nomura, S. Fujii, K. Kanaya, H. Matsuda, "Oxygen- or sulphur- containing organoindium compounds for precursors of indium oxide and sulphide thin films", Polyhedron, **9**, p. 361, 1990.

[18] R. Nomura, Y. Sekl, H. Matsuda, "Preparation of copper indium sulfide ($CuInS_2$) thin films by single-source MOCVD process using $Bu_2In(SPr-iso)Cu(S_2CNPr-iso_2)$", J. Mater. Chem. **2(7)**, p.765, 1992.

[19] R. Nomura, Y. Sekl, H. Matsuda, "Preparation of copper indium sulfide ($CuIn_5S_8$) thin films by single-source organometallic chemical vapor deposition", Thin Solid Films, **209(2)**, p. 145, 1992.

[20] W. Hirpo, S. Dhingra, A. C. Sutorik, M. G. Kanatzidis, "Synthesis of mixed Copper-Indium chalcogenolates. Single Source Precursors for the photovoltaic material $CuInQ_2$ (Q = s, Se)", J. Am. Chem. Soc., **115**, p. 597, 1993.

[21] J. A. Hollingsworth, A. F. Hepp, W. E. Buhro, "Spray CVD of Copper Indium Disulfide Films: Control of Microstructure and crystallographic orientation", Chem. Vap. Deposition, **5**, p. 105, 1999.

[22] J. A. Hollingsworth, W. E. Buhro, A. F. Hepp, P. P. Jenkins, M. A. Stan, "Spray chemical vapor deposition of $CuInS_2$ thin films for application in solar cell devices", Mat. Res. Soc. Symp. Proc., **495**, p 171, 1998.

[23] J. A. Hollingsworth, "Chemical routes to nanocrystalline and thin-film III-VI and I-III-VI semiconductors" PhD Thesis, Supervisor W. E. Buhro, Washington University1999.

[24] R. Raffaelle, S. Castro, S. G. Bailey, "Quantum Dots Solar Cells", XVII Space Photovoltaic Research and Tech. Conf., 2001.

[25] J. D. Harris, D. G. Hehemann, J. E. Cowen, A. F. Hepp, R. P. Raffaelle, J. A. Hollingsworth, "Using single source precursors and spray chemical vapor deposition to grow thin-film $CuInS_2$", Proc. Of the 28th IEEE Photovoltaic Specialists Conference, Anchorage, AK, p. 563, 2000.

[26] R. S. Drago, N. Wong, C. Bilgrien, G. C.Vogel, "E and C parameters from Hammett substituent constants and use of E and C to understand cobalt-carbon bond energies", Inorg. Chem. **26(1)**, p. 9, 1987.

[27] TA Instruments, "Thermal Analysis & Rheology; Chapter 3 Running Experiments: Preparing Samples", p.3, 1998.

[28] J. E. Cowen, A. Riga, A. F. Hepp, S. Duraj, K. K. Banger, R. MaClaron, NATAS Conference Session: Thermal Application of Materials; NATAS Conference St. Louis, MO (2001).

[29] K. K Banger, J. Harris, J. Cowen, A. F. Hepp, E-MRS Spring Meeting, Symposium P: Thin Film Materials for Photovoltaics, Strasbourg, France, 2001.

[30] K. Siemwe, J. Klaer, I. Luck, D. Braunig, "Influence of crystal Orientation on Device Performance of $CuInS_2$ solar cells", Proc. Of the 28th IEEE Photovoltaic Specialists Conference, Anchorage, AK, p. 630, 2000.