



Single Source Precursors for Thin Film Solar Cells

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Acknowledgments

We would like to acknowledge the collaboration of scientist and researchers from Government, Industry, and University laboratories who have helped in the development of this project. In addition, we gratefully acknowledge National Aeronautics and Space Administration (NASA) for financial support under cooperative agreements NCC3-817, NCC3-563, and NCC3-734.

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SINGLE SOURCE PRECURSORS FOR THIN FILM SOLAR CELLS

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INTRODUCTION

The development of thin film flexible lightweight solar cells is of high importance for both terrestrial and space applications. Thin film solar cells use 30-100 times less semiconducting material and are less expensive to manufacture than conventional crystalline silicon cells. Current thin film photovoltaic (PV) research encompasses development of CdTe, Cu(Ga:In)(S:Se)₂ (CIS) and thin film silicon based solar cells. One of the most promising technologies lies in the development of polycrystalline thin films,¹ due to their ease of manufacture and importantly, their lightweight structure enables them to achieve higher specific power (WKg⁻¹), than alternative single crystalline devices.²

With the increasing cost of launching payloads into space, currently estimated to be approximately \$20k per Kg, lightweight materials for space power systems are now being considered. Use of flexible solar cells will be mission enabling for several proposed NASA space programs, which allows for efficient storage in launch vehicles for later controlled deployment in space (Figure 1). Similarly, for terrestrial applications, thin film photovoltaics are highly appealing due to their flexible lightweight construction, permitting them to be "molded" onto non-rigid, or uniform structures for recreational or innovative power systems.

Photovoltaic modules based on ternary chalcopyrite absorber layers, (I-III-VI₂; Cu(In:Ga)(S:Se)₂) have been the focus of intense investigation for over two decades. The use of chalcopyrite absorbers are highly appealing since their bandgaps correlate well to the maximum photon power density in the solar spectrum for both terrestrial (AM 1.5), and space applications (AM0) (Figure 2), while displaying long term stability and excellent radiation tolerance.^{3,4} Additionally, by adjusting the percent 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.⁵

One of the key technical issues outlined in the 2001 US Photovoltaic roadmap is the need to develop low cost, high throughput manufacturing for high-efficiency thin film solar cells. Thus, a key step for device fabrication for thin film solar cells is the deposition onto flexible, lightweight substrates such as polyimides. Current methods for depositing ternary crystallite compounds include co-evaporation of elements,⁶⁻⁸ or alloys,⁹ electrodeposition,¹⁰ reactive-sintering,¹¹ and flash evaporation,¹² which are often followed by toxic sulphurization/selenization steps, at elevated temperatures. Furthermore, under these conditions loss of volatile In/Ga chalcogenides is common.^{6,13} The high temperature requirements makes this protocol incompatible with all presently known flexible polyimides, or other polymer substrates. In addition, the 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, stoichiometric control of deposited films can be difficult to achieve and film contamination has been reported.^{14,15} A novel alternative approach is the use of ternary single source precursors, (SSP's), which have the I-III-VI₂ stoichiometry "built in" and are suitable for low temperature deposition (Figure 3). Although, a rich and diverse array of binary SSP's¹⁶⁻¹⁹ are known, characterized, reviewed and tested, the number of known ternary SSP's is limited, as is their use in deposition processes.¹⁶ Hence, it is the goal of this account to highlight recent advances carried out at our labs and other groups, summarizing a highly promising technique for thin film growth, via molecular design of single source precursors for use in a CVD process.

Spray CVD

Spray CVD has become an advancing technique where a room-temperature precursor solution is ultrasonically nebulized, and is swept into a two-zone, hot-wall reactor (Figure 4). The carrier-solvent is evaporated in the warm zone, and the gaseous precursors are decomposed in the hot zone, where film growth occurs as in conventional CVD. Spray CVD maintains the most desirable features of MOCVD and spray pyrolysis, such as film growth in inert atmospheres, large area deposition, laminar flow over the substrate, and low temperature solution reservoir, while avoiding the major difficulties of each.^{20,21} It minimizes the high volatility and temperature requirements for the precursor, which are essential in MOCVD, by delivering the precursor to the furnace as an aerosol propelled by a fast-flowing carrier gas from a low-temperature precursor reservoir analogous to that employed in spray pyrolysis. The latter feature is an important benefit that can prevent premature precursor decomposition when using thermally labile precursors.

PREVIOUS WORK

In early studies Nomura *et al*, reported that an equimolar mixture of $[\text{Bu}^i_2\text{InSPr}]$ and $[\text{Cu}(\text{S}_2\text{CNBu}_2)_2]$ decomposed to afford CuInS_2 powders.²² 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 $[\text{Bu}^i_2\text{InSPr}]$ and $[\text{Cu}(\text{S}_2\text{CNBu}_2)_2]$ (as used in solution pyrolysis) afforded the single source precursor $[\text{Bu}_2\text{In}(\text{SPr}^i)\text{Cu}(\text{S}_2\text{CNPr}^i_2)]$ before decomposing to the chalcopyrite matrix.²³ Analytical and spectral data confirmed that the mixture of $[\text{Bu}^i_2\text{InSPr}]$ and $[\text{Cu}(\text{S}_2\text{CNBu}_2)_2]$ yielded a SSP. A number of analogous ternary CIS precursors were also synthesized by the reaction of alkyl indium thiolates with copper dithiocarbamates [Eq.1].²⁴ However, only $[\text{Bu}_2\text{In}(\text{SPr}^i)\text{Cu}(\text{S}_2\text{CNPr}^i_2)]$ was successfully implemented for depositing pure CuInS_2 by low pressure MOCVD. In the case of $[\text{BuIn}(\text{SPr}^i)_2\text{Cu}(\text{S}_2\text{CNR}^i_2)]$, tetragonal CuIn_5S_8 was deposited [Eq.2].²⁵

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.3].²⁶ Pyrolysis studies undertaken revealed that the Se derivative could be converted into CuInSe_2 at 400-450 °C @ 0.01 mm Hg [Eq.4], but none of the precursors had been evaluated in a thin-film deposition study.

In continuing work, Buhro and Hepp were able to demonstrate that $[\{\text{PPh}_3\}_2\text{Cu}(\text{SEt})_2\text{In}(\text{SEt})_2]$ could be utilized in a spray CVD process, for depositing thin-film CuInS_2 below 400 °C.^{27,28,29} Thin films were 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 were 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 confirmed the deposited CuInS_2 thin films were direct bandgap semiconductors.

In the course of our investigations for improved single source precursors for the spray CVD of chalcopyrite thin-films, to the ternary semiconductor $\text{Cu}(\text{Ga:In})(\text{Se:S})_2$, we have continued to expand the molecular design of SSP based on the $[\{\text{LR}_3\}_2\text{Cu}(\text{ER}')_2\text{M}(\text{ER}')_2]$ architecture.²⁶ 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 (Figure 5).

CHEMICAL SYNTHESIS

The SSP 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 with NaOEt in methanol^{30,31} (Scheme 1). 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 ($L \rightarrow Cu$)
- 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,³² 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's of good "leaving ability", would promote the facile release of the chalcogenide.

CHARACTERIZATION

Initial studies focused on basic modification of the SSP's, 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 6a).

A further example of the flexibility of the $[\{LR_3\}_2Cu(YR')_2M(ER')_2]$ architecture to direct adjustment of these precursors are the SSP **7** and **8**, which represent the first liquid single source precursors for the deposition of $CuInS_2$.³⁰ 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 and 5 °C/min.³³ In low temperature DSC experiments using controlled and quench 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 (Figure 7).

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 represent 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.¹⁶ In addition, preliminary Vacuum-TGA studies for the “smoothed” profile for the SSP **7**, shows the extrapolated onset can be lowered by approx 80 °C thus lowering the degradation temperature window and making these precursors highly suitable for use in low temperature/pressure spray CVD on space qualified substrates such as Kapton™ (Figure 6b). Remarkably both liquid precursors show excellent solubility in both polar and non-polar solvents, which can be attributed to their ionic structure and the non-polar alkyl groups resident on the tertiary phosphine.

The ability of the new precursors 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. Furthermore, using TGA-Evolved Gas Analysis, the volatile components from the degradation of the SSP's could be analyzed via real-time FTIR and mass spectroscopy, thus providing information for the decomposition mechanism.³⁴ The real time FTIR spectrum for **7** and **8** shows absorptions at approx 3000, 1460, 1390, 1300 and 1250 cm⁻¹ (Figure 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 9a). 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 than 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 (Figure 9b). Thus, the use of TGA-EGA provides conclusive evidence for the mechanism of decomposition for the single source precursors to occur via the initial loss of a chalcogenide moiety, followed by loss of the neutral donor ligand.

XRD spectra for the non-volatile material produced from the pyrolysis of **7** with the JCPDS reference patterns for CuInS₂ (27-0159), confirmed it to be single-phase CuInS₂ (Figure 10). 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.

The preparation of the first SSP to the semiconductor CuGaS₂ was also investigated.³¹ Although the molecular structure for SSP **9** was not fully characterized, its suitability to afford bulk and thin film CuGaS₂ was studied by TGA (Table 1) and XRD. In addition, the optical properties of the deposited thin-films were also investigated. Powder XRD analysis on the non-volatile

product from bulk pyrolysis, (N₂, 600 °C), confirmed the collected material to be single-phase 112 oriented CuGaS₂ (Figure 11), having an average coherence length of 28 nm.

THIN FILM STUDY

Well adhering films of CuInS₂ were deposited on a Molybdenum substrate by spray CVD at 390°C using [PBu_3]₂Cu(SEt)₂In(SEt)₂, which were dark blue/black, due to variation in film thickness. As deposited, the CuInS₂ film is highly (112) oriented (Figure 12), which is ideal, since the preferred orientation for CIS films used in photovoltaic devices is (112) as these films have a low series resistance.³⁵

Measurements of the EDS emission 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 CuInS₂ (Table 2), and no evidence of phosphorous or carbon contamination could be detected, verifying the precursor decomposes cleanly as evidenced in EGA-TGA studies.

Unfortunately due to the limited quantities of the liquid precursor for thin film deposition, 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 have been shown to make excellent Schottky barriers³⁶ (Figure 13). The electrical properties of the deposited films, were evaluated by current verses voltage (IV) measurements recorded for the thin films using thermally evaporated aluminum contacts (10 μm²), to make Schottky barrier diodes (Figure 14).

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 is 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.

Spray CVD deposition studies utilizing the new Ga SSP 9, in a toluene/CH₂Br₂ solution (0.01 M:86 vol % toluene; 1.3 mmol; SSP 9) afforded well-adhered dense thin film, (450 ± 5 °C, 4.0 L/min). The films were visually smooth and optically transparent exhibiting a pink and green surface tint. XRD analysis confirmed the film to be highly 112 oriented, tetragonal single phase CuGaS₂ (Figure 15).

The 220/204 reflections and the 312/116 reflections were split consistent with the tetragonal distortion of the crystal lattice³⁷ (Figure 15). Lattice parameters *a* and *c* were calculated from X-ray *d* spacings according to Eq. 5 where *h*, *k*, and *l* refer to the Miller indices of individual reflections.³⁸ The *d* spacing of the 220 reflection was used to calculate *a*, and the *d* spacing of the 112 reflection was used with the calculated lattice parameter *a* to determine *c*. The lattice parameters, *c/a* ratio, and the distortion parameter *x* (where $x = 2 - c/a$, given that a hypothetical *c/a* ratio of 2 would result in the *absence* of any tetragonal distortion) are presented in Table 3. Comparison of the data collected from the CuGaS₂ thin film shows they are in good agreement

with the JCPDS reference values for single-crystal CuGaS₂ and with those reported in literature.³⁹

SEM images reveal the films are dense with an average grain size of 410 nm, and oriented predominantly in a vertical manner (Figure 16c-d). The surface microstructure consisted of faceted grains many of which exhibited a trigonal shape (Figure 16a-b), which occurs as a result of close-packed intersecting (112) faces of the chalcopyrite lattice. These are the lowest surface-energy faces and typically control chalcopyrite morphology.^{19,40} The grain sizes observed by SEM are considerably larger than the average coherence lengths calculated from X-ray line broadening, which could have been reduced by a high defect density in the grains or by strain in the film.

Sheet resistivity for the CuGaS₂ thin film samples were determined using the four-point probe method.⁴¹ Sheet resistance was calculated from current-voltage data (Figure 17) by $R_s = K_p V/I$, where K_p is a constant, (for a probe of the type used here and for a sample with planar dimensions that can be considered infinite relative to the probe spacing, $K_p = \pi/\ln 2$). The resistivity determined for the film deposited at 450 °C on fused silica, was found to be 1.56(4) Ω·cm, which is comparable to the low resistivity value of 1.0 Ω·cm obtained from melt-grown single-crystal CuGaS₂ (S-annealed).⁴¹

The optical bandgap of the films were determined from optical transmittance data, which showed the film to absorb incident light below 480 nm (Figure 18a). Transmittance was observed to change most dramatically in the region from 480–540 nm, which is the region of the direct absorption edge. Calculation of the derivative for the transmission curve provided a more precise method to determine the band gap within this region,⁴² yielding a maxima at 2.42 eV (Figure 18b). This value is in very good accord with the known direct band gap of CuGaS₂, $E_g = 2.43$ eV as reported in literature.⁴³

Initial studies using the two analogous Ga and In SSP for fabrication of an alloy film, Cu(In:Ga)S₂, in a dual-source spray CVD were also investigated. A film was deposited from a mixed toluene solution of [Ph_3P]₂Cu(μ -SEt)₂In(SEt)₂ **1** (0.0075 M) and the Ga analog **9** (0.0025 M).³¹ Although a thin-film was deposited, composition and microstructure varied along the length of the thin film. XRD reflections representing the 112 planes were broad and complicated by the presence of an unidentified reflection in that region. The 220/204 planes was represented by a single, unresolved reflection that yielded an average grain size of ~40 nm. The relative contribution of Ga and In to the multinary structure was determined by comparing the 2-theta values for this reflection in the multinary pattern to those in the patterns of the ternary end-members, CuInS₂ and CuGaS₂ (Figure 19). The composition of each metal was assumed to vary linearly with 2-theta from 100 % In to 100 % Ga based on Vegard's Law. The tetragonal splitting was neglected in the CuGaS₂ pattern by averaging the 2-theta values for the 220 and the 204 reflections.

The atomic percent of Ga in the film was found to increase along this length from the front to rear of the film. The film deposited in the first centimeter had a composition of CuIn_{0.43}Ga_{0.57}S₂, in the middle; CuIn_{0.38}Ga_{0.62}S₂, whilst that deposited in the last centimeter had the highest contribution of Ga; CuIn_{0.27}Ga_{0.73}S₂. A uniform composition over large areas was therefore not

achieved, and, interestingly, none of the compositions were close to the expected $\text{In}_{0.75}\text{Ga}_{0.25}$ ratio in accord with the precursor molar ratio. SEM images of the films (Figure 20) revealed the microstructure was similar to that observed for CuInS_2 deposited at $450\text{ }^\circ\text{C}$.²⁸ The variation in film composition is understandable since the two precursors thermal decomposition profiles are unlike. Therefore, using two SSP's with matching thermal profiles can provide an effective means for depositing multi-ternary films.

SUMMARY AND OUTLOOK

The versatility of the $[\{\text{LR}_3\}_2\text{Cu}(\text{ER}')_2\text{M}(\text{ER}')_2]$ architecture is clearly demonstrated by the preparation of SSP's to multi-ternary semiconductors. Thermal analysis data substantiates that steric and electronic molecular modification on either the neutral donor, or chalcogenide, permits directed adjustment of the solid-state phase and stability of the precursors. Evolved gas analysis, confirms the mechanism of decomposition for the SSP's proceeds "cleanly" by the loss of the chalcogenide moiety, followed by loss of the neutral donor. Spray CVD using SSP's is a mild, simple, clean, and scalable technique for depositing CuInE_2 or CuGaE_2 ($\text{E} = \text{S}, \text{Se}$) thin-films on flexible polymer substrates at reduced temperatures. Although tests for the deposition of the wide bandgap alloy $\text{Cu}(\text{Ga:In})\text{S}_2$, led to a non-homogenous film composition, it is evident the use of two SSP's with similar thermal profiles, consistent film stoichiometry can be achieved.

Clearly the full potential of CIS PV devices has not been fully exploited since the combination of group I-III-VI₂ elements can result in a variety of end products. Therefore standards need to be defined which can associate device processing, fabrication, film composition etc. to cell band-gap and efficiency. Spray CVD in conjunction with SSP design provides a proof-of-concept for a reproducible high manufacturability process. An outlook for further investigation that needs to be undertaken is; (1) **Precursor Design:** Development of more volatile/thermally labile systems. This can be achieved by the incorporation of fluorinated, or silylated function groups. Importantly due to the high propensity of fluorine by silicon, incorporation of both elements in the molecule can serve not only to increase volatility, but also as a "self-cleaning" mechanism should not precursor decompose in undesired pathway. (2) **Processing Parameters:** Spray CVD has a number of tunable variables, such as droplet size, flow-rate, concentration, solvent polarity, which is advantageous to achieve the desired film characteristics. Thus an in-dept study needs to address these parameters to film composition. (3) **Device fabrication:** working devices from deposited films need to be tested to aide SSP design and spray CVD process parameters. The work reported here on the molecular design of SSP's for their use in a spray CVD process although still in its infancy, undoubtedly shows it as a mass producible, cost effective method for fabricating commercial thin film PV devices.

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FIGURE 1. Lightweight flexible PV array.

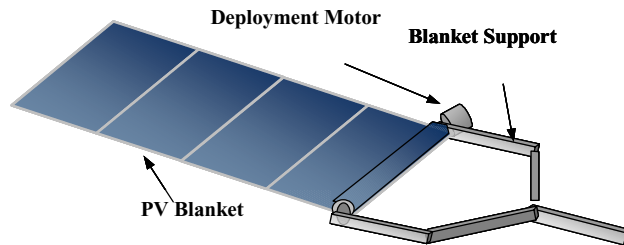


FIGURE 2. Predicted efficiency versus bandgap for thin-film photovoltaic materials for solar spectra in space (AM0) and on the surface of the Earth (AM1.5) at 300K compared with bandgaps of other PV materials with unconcentrated ($C = 1$) and high concentration ($C = 1000$) sunlight.

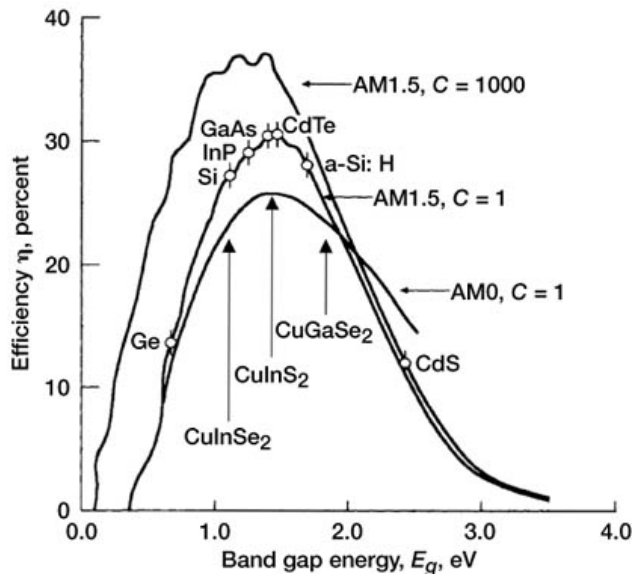


FIGURE 3. Pyrolysis of SSP [$\{\text{PPh}_3\}_2\text{Cu}(\text{SEt})_2\text{In}(\text{SEt})_2$], to afford the semi-conductor CuInS_2 .

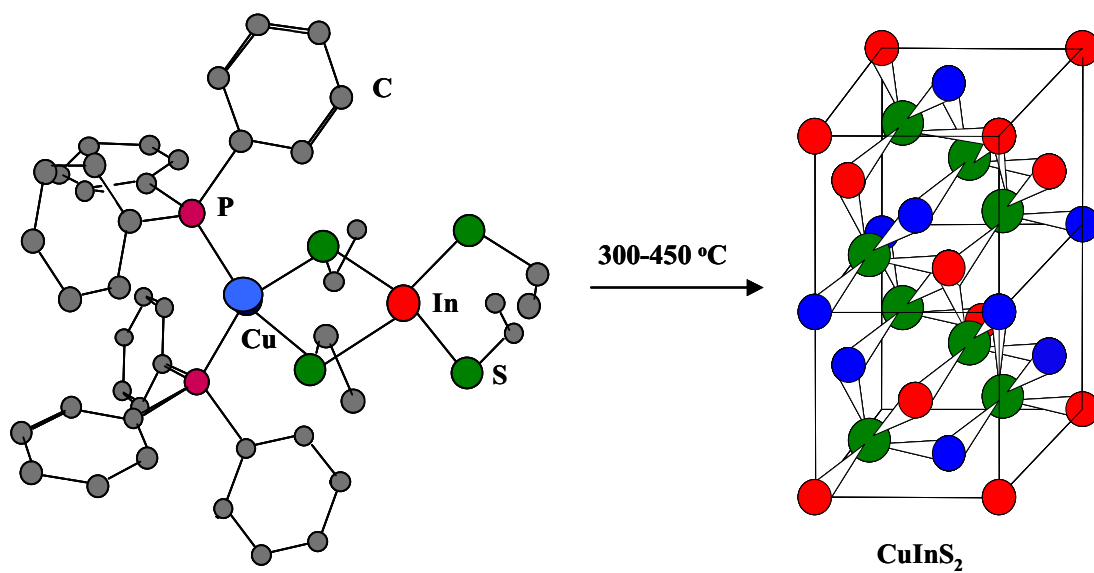


FIGURE 4. Schematic for spray CVD apparatus.

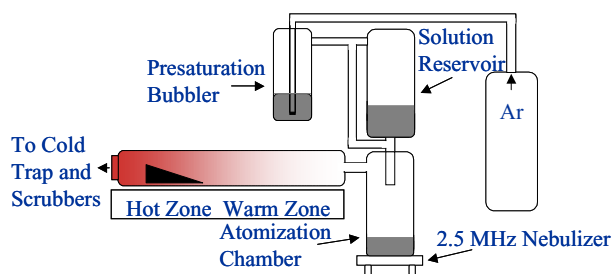


FIGURE 5. Single crystal structure of $[\{PPh_3\}_2Cu(SET)_2In(SET)_2]$,²⁶ indicating “tunable” sites.

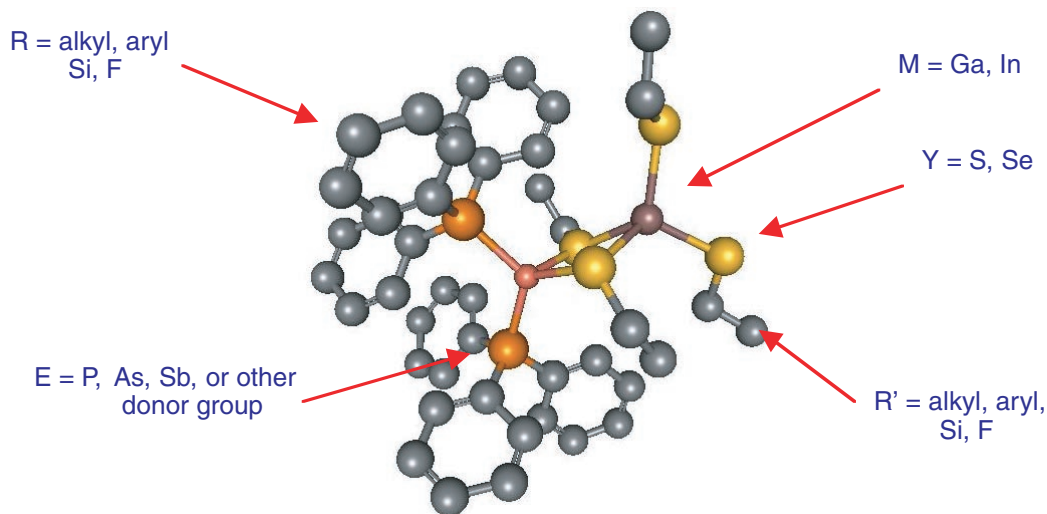


FIGURE 6. TGA profiles for $[\{P(n-Bu)_3\}_2Cu(SET)_2In(SET)_2]$, 7.

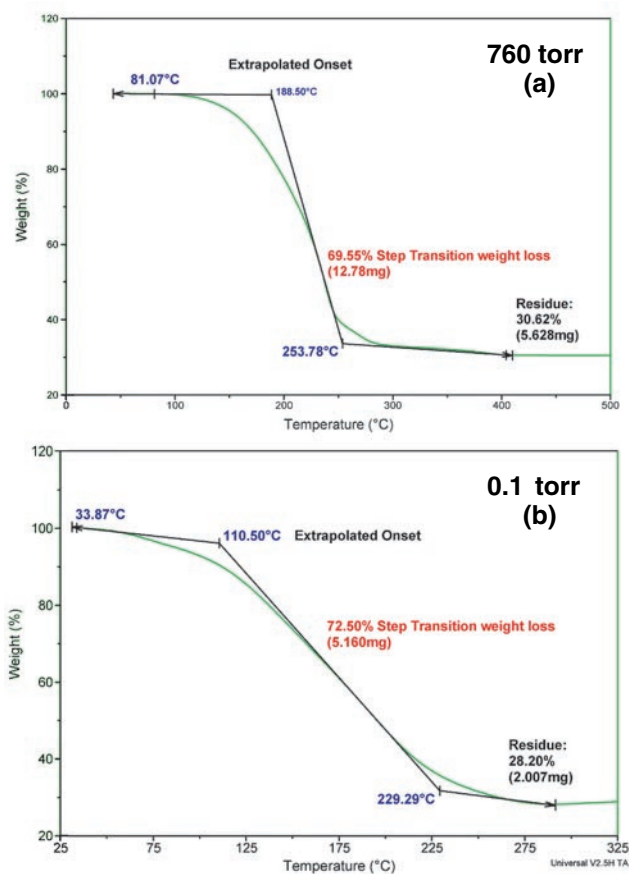


FIGURE 7. Low temperature DSC for $[\{P(Bu^n)_3\}_2Cu(SEt)_2In(SEt)_2]$ **7** and $[\{P(Bu^n)_3\}_2Cu(SPr^n)_2In(SPr^n)_2]$ **8**.

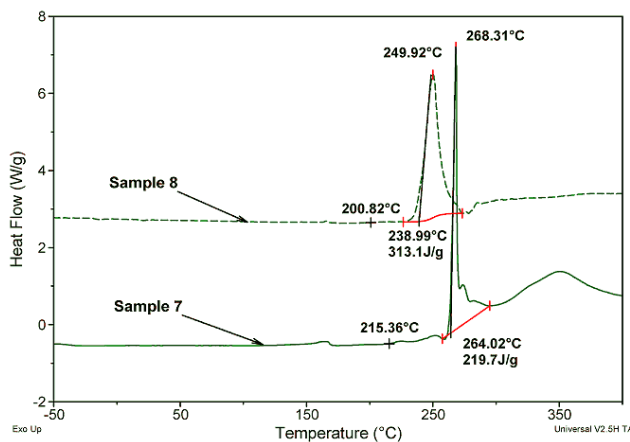


FIGURE 8. EGA-FTIR spectra for $[\{P(n-Bu)_3\}_2Cu(SEt)_2In(SEt)_2]$ **7** and $[\{P(n-Bu)_3\}_2Cu(SPr^n)_2In(SPr^n)_2]$, **8**.

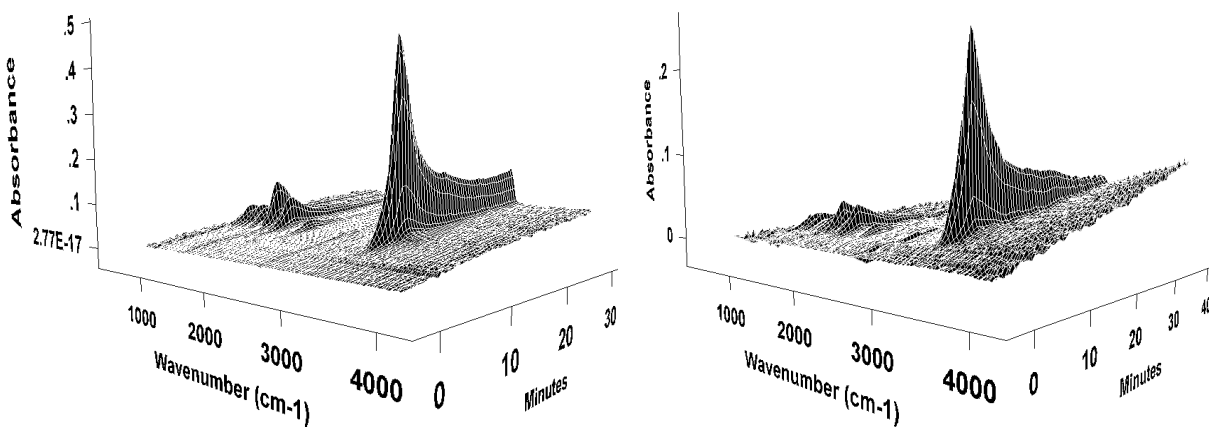


FIGURE 9. EGA-MS (EI) data for $[\{P(n\text{-Bu})_3\}_2\text{Cu}(\text{SEt})_2\text{In}(\text{SEt})_2]$, **7**.

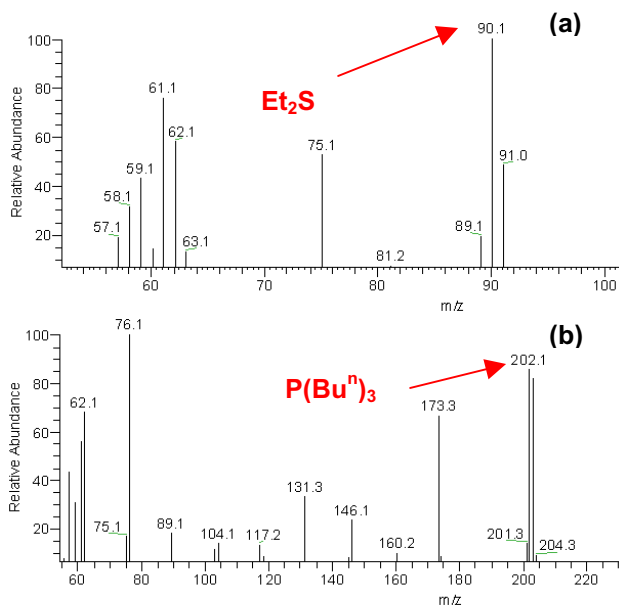


FIGURE 10. XRD Powder Diffraction for non-volatile residue from pyrolysis of $[\{P(n\text{-Bu})_3\}_2\text{Cu}(\text{SEt})_2\text{In}(\text{SEt})_2]$, (Cu $K\alpha$, 1.541 Å).

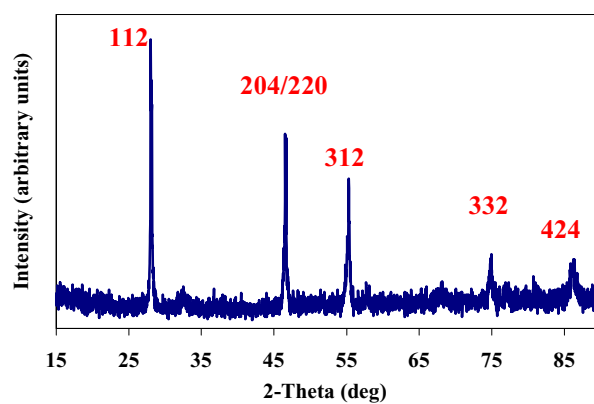


FIGURE 11. XRD pattern of non-volatile solid obtained from bulk pyrolysis of $[(\text{Ph}_3\text{P})_2\text{CuGa}(\text{SEt})_x] \mathbf{9}$ (600 °C, 300 min.). All reflections correspond to gallite CuGaS_2 (JCPDS # 25-0279).

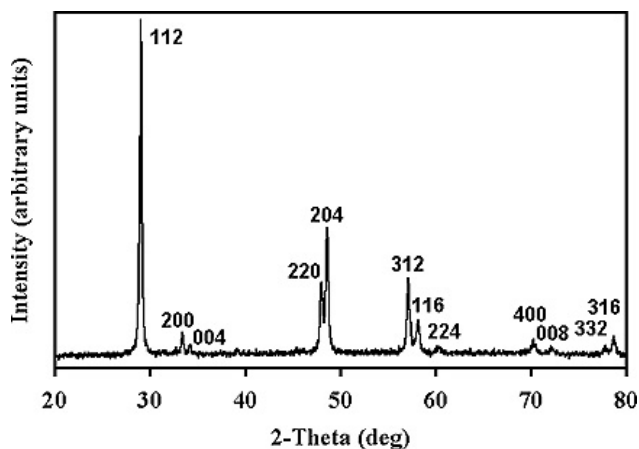


FIGURE 12. X-ray powder diffraction spectra of a CuInS_2 thin film on Mo using SSP 7.

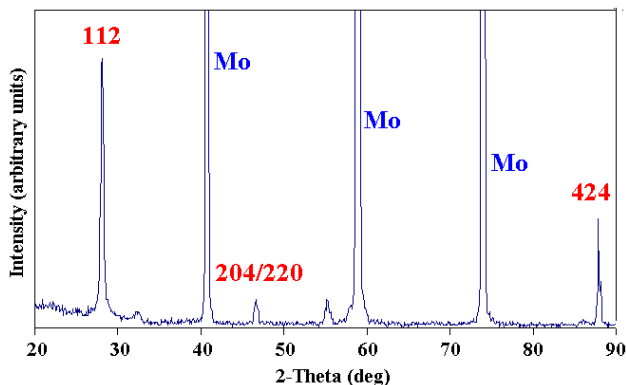


FIGURE 13. SEM of deposited CIS film using $[\{\text{P}(\text{PPh})_3\}_2\text{Cu}(\text{SEt})_2\text{In}(\text{SEt})_2] \mathbf{1}$.

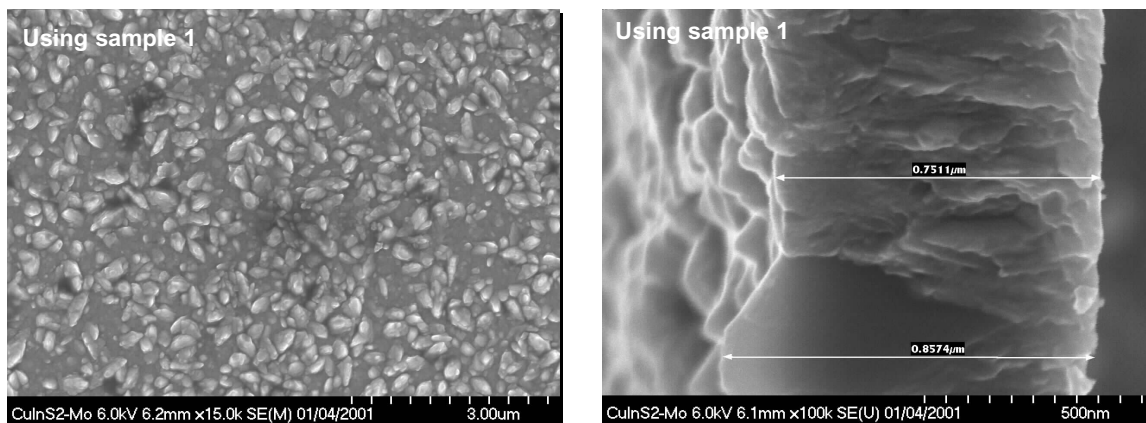


FIGURE 14. Current density vs. voltage plot of Schottky barrier made from evaporated Al on CuInS₂ on Mo foil using SSP 1.

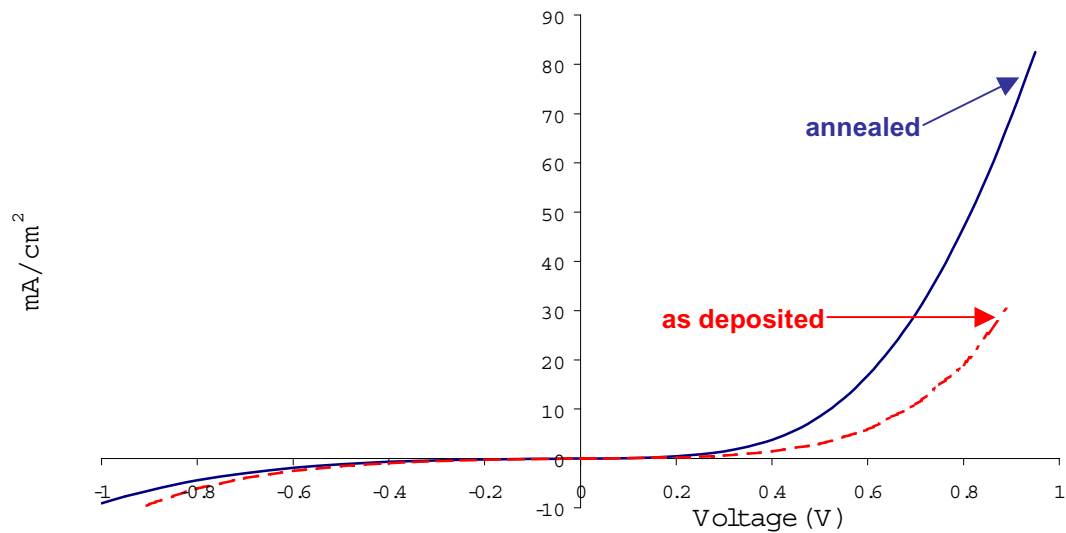


FIGURE 15. XRD pattern of spray-CVD grown CuGaS₂ film on Si(111), using SSP 9. Reflections correspond to those reported for Gallite in JCPDS reference # 25-0279.

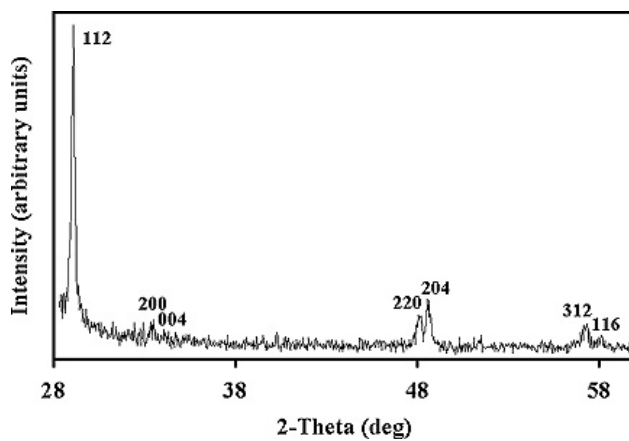


FIGURE 16. SEM images of CuGaS₂ films deposited by spray CVD. a) surface view showing crystalline, faceted, approximately-equiaxed grains. b) Surface view; 30° tilt showing triangular shape of many of the grains characteristic of 112-oriented crystals. c) and d) edge views showing roughly columnar crystal-growth pattern and dense nature of the film. Triangular grains protruding from the film surface are visible in c).

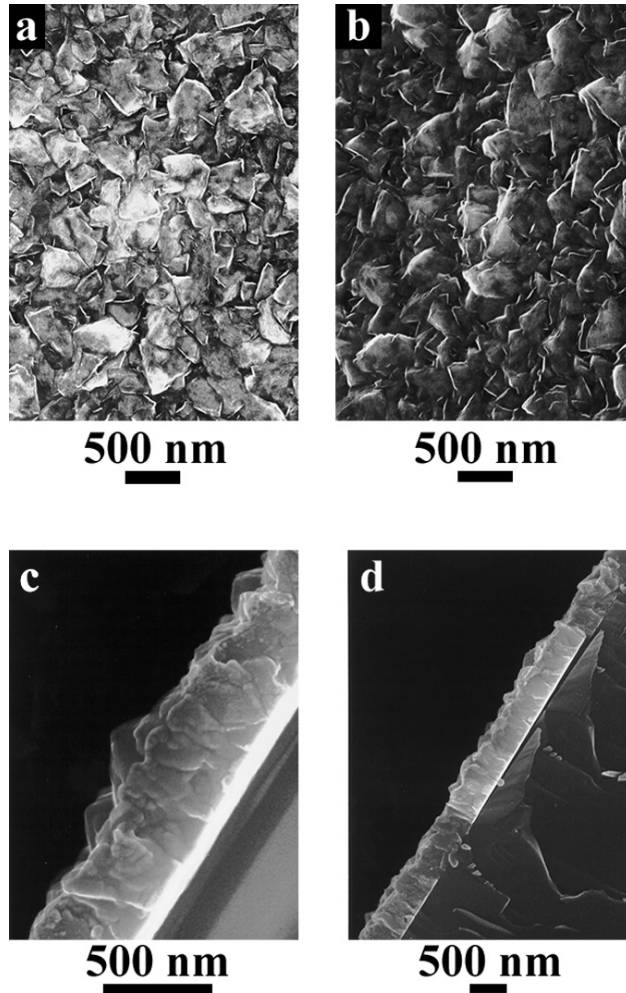


FIGURE 17. V-I curve for CuGaS₂ thin film. The linear region below 3.0 E-05 was used to calculate sheet resistance.

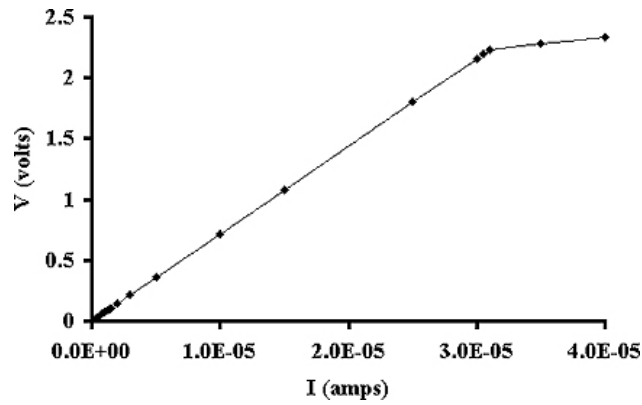


FIGURE 18. a) Transmittance vs. wavelength for CuGaS₂ thin film; (I = transmitted power, I₀ = incident power; b) Plot of the derivative of the transmission data vs. energy.

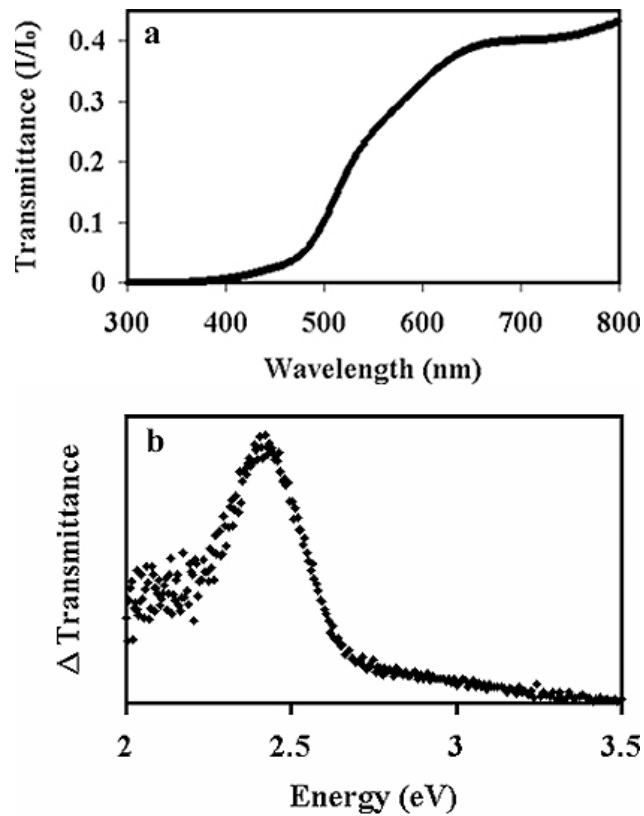


FIGURE 19. XRD spectra highlighting the 220/204 reflections of a CuGaS_2 film (bottom; $T_s = 450^\circ\text{C}$), a CuInS_2 film (top; $T_s = 400^\circ\text{C}$) and alloy films having In_xGa_y contents in the range: $\text{In}_{0.43}\text{Ga}_{0.57} - \text{In}_{0.27}\text{Ga}_{0.73}$. All films were deposited on fused silica.

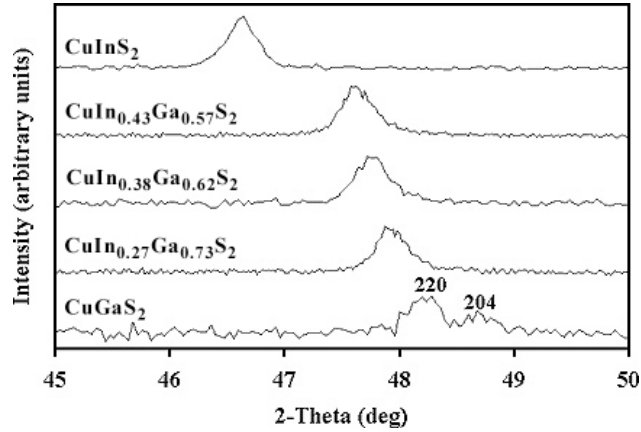
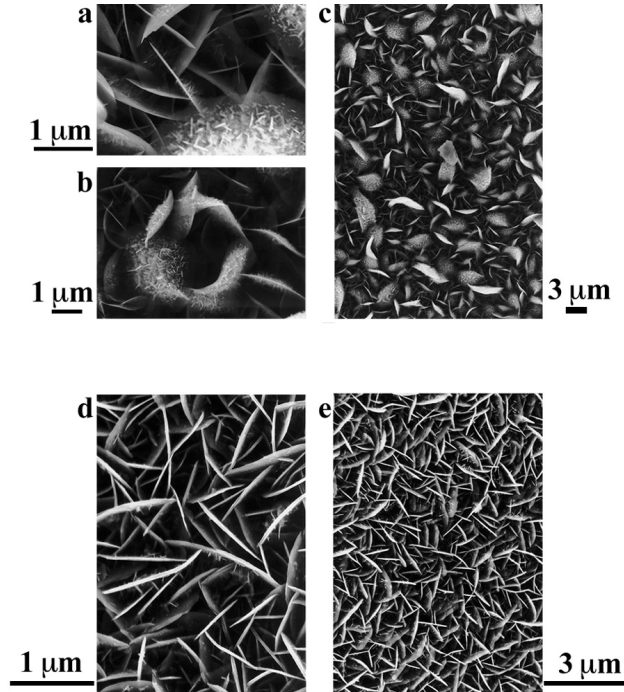
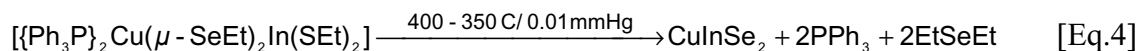
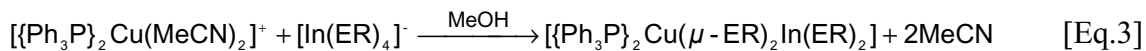
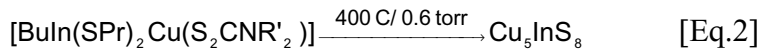
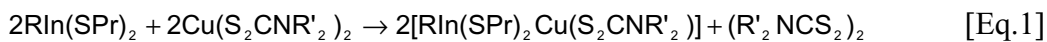


FIGURE 20. SEM images of the alloy film showing the variation in microstructure with composition. a – c) Film deposited in the first centimeter: $\text{CuIn}_{0.43}\text{Ga}_{0.57}\text{S}_2$. d and e) Film deposited in the last centimeter: $\text{CuIn}_{0.27}\text{Ga}_{0.73}\text{S}_2$.

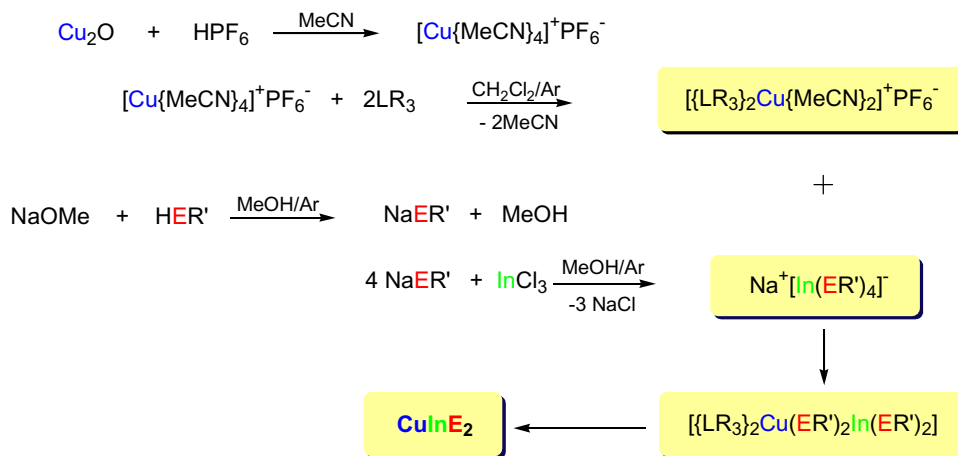


EQUATIONS and SCHEMES



$$1/d^2 = 1/a^2 (h^2 + k^2) + l^2/c^2 \quad [\text{Eq.5}]$$

SCHEME 1. Synthesis of ternary single source precursors



$\text{L} = \text{P}, \text{As}, \text{Sb}; \text{E} = \text{S}, \text{Se}; \text{R}' \text{ \& R} = \text{alkyl}, \text{aryl}$

TABLES

TABLE 1. Thermal data for ternary Single Source precursors.

| Single Source Precursors | TGA | | | DSC | |
|---|---------------------|------------------|--------------|--------------|---------------|
| | Extrap. Onset °C | MRW °C / % | Residue % | M.P. °C | Decomp. °C |
| 1 [$\{PPh_3\}_2Cu(SEt)_2In(SEt)_2$] | 236 | 269 | 25 | 122 | 266 |
| 2 [$\{AsPh_3\}_2Cu(SEt)_2In(SEt)_2$] | 205 | 233 | 18 | 47 | 276 |
| 3 [$\{SbPh_3\}_2Cu(SEt)_2In(SEt)_2$] | 212 | 239 | 26 | 45 | 271 |
| 4 [$\{PPh_3\}_2Cu(SPr^i)_2In(SPr^i)_2$] | 215 | 254 | 29 | 163 | 260 |
| 5 [$\{PPh_3\}_2Cu(SPh)_2In(SPh)_2$] | 261 | 325 | 22 | 117 | 280 |
| 6 [$\{PPh_3\}_2Cu(SePh)_2In(SePh)_2$] | 223 | 253 | 22 | 53 | 219 |
| 7 [$\{P(Bu^n)_3\}_2Cu(SEt)_2In(SEt)_2$] | 189 | 238 | 31 | - | 264 |
| 8 [$\{P(Bu^n)_3\}_2Cu(S(Pr^n))_2In(SPr^n)_2$] | 171 | 225 | 29 | - | 239 |
| 9 [$\{PPh_3\}_2CuGa(SEt)_x$] ^a | ^b | 310 ^c | 25 | ^b | ^b |

^astructure not elucidated (x=3, or 4), ^bnot recorded.

TABLE 2. 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 |

TABLE 3. Comparison of thin-film and single-crystal $CuGaS_2$ lattice parameters, a and c , c/a , and the distortion parameter x .

| a (Å) | c (Å) | a/c | x | Thin film fabrication method |
|---------|---------|--------|--------|---|
| 5.353 | 10.495 | 1.9606 | 0.0394 | Spray-CVD deposited film |
| 5.35 | 10.48 | 1.959 | 0.0410 | Evaporated film ³⁹ |
| 5.351 | 10.484 | 1.9593 | 0.0407 | JCPDS card 25-0297: single crystal prepared from the elements |

BIOGRAPHICAL INFORMATION

Kulbinder Banger received his Ph.D. in Organometallic Fluorine Chemistry from the University of Manchester Institute of Science and Technology, UK (1998), under the guidance of Dr. A. Brisdon. During which time he was awarded the Proctor & Gamble award for Research. After completing his postdoctoral fellowship at the University at Albany, NY with Dr. J. Welch, he was employed as a Scientist at the New York State Center For Advanced Thin-film Technology, Albany, NY (1999). Kulbinder is currently working as a Senior Research Associate for Ohio Aerospace Institute conducting research at NASA GRC, developing thin-film solar cells, polymer electrolytes, and new CVD precursors.

Jennifer Hollingsworth received her Ph.D. in Materials Inorganic Chemistry in 1999 from Washington University in St. Louis, MO, conducting her graduate work as a NASA Graduate Student Researchers Program Center Fellow. Jennifer is currently a Technical Staff Member of the Chemistry Division of Los Alamos National Lab (LANL), coming to the Lab in 1999 as a Director's Funded Postdoctoral Fellow. Her current research interests include development of new nanostructured materials (nanocrystal-quantum-dot based) for application in optoelectronics, telecommunications, sensors, and artificial photosynthesis.

Jerry D. Harris earned his B.S. from Northwest Nazarene University (1991) and his Ph.D. from Texas A&M University (1997). He was a Kent State University postdoctoral appointee to NASA Glenn Research Center prior to joining Cleveland State University. He still actively collaborates with NASA GRC scientist's in the areas of thin film photovoltaics and thin film battery materials. Currently he is developing new fabrication techniques for the deposition of solar cell materials via spray CVD, in addition to more efficient dye sensitized solar cells.

Jonathan Cowen is an undergraduate student studying chemistry at Cleveland State University. In 1999 he joined the Thin Film Technologies group, led by Dr. Aloysius Hepp, at NASA Glenn Research Center. In the fall of 2000 he received the ACS-Lubrizol award (Cleveland district) for undergraduate research in Inorganic chemistry for his work at NASA Glenn and CSU. Jonathan is expected to complete his B.S. in the summer of 2002.

William Buhro received his Ph.D. from UCLA in 1985 and was awarded the Chester Davis Research Fellowship, (1985). He is currently a faculty member at Washington University St. Louis and has been the recipient of a number of awards, including Faculty Award for Teaching, (1990), NSF Presidential Young Investigator Award, (1991-1996), Emerson Electric Co. Excellence in Teaching Award, (1996) and Washington University Faculty Award for Teaching, (1996). His current research focuses on synthetic and mechanistic materials chemistry, nanocomposite and nanocrystalline materials.

Aloysius F. Hepp earned a Ph.D. in Chemistry in 1983 at MIT with Prof. Mark Wrighton in Organometallic Photochemistry. Dr. Hepp has been a Senior Scientist at NASA Glenn Research Center's Photovoltaic and Space Environments Branch for 15 years and is responsible for Thin Film Photovoltaics; he is a recipient of the NASA Exceptional Achievement Medal. His research focuses on chemical synthesis and thin film deposition technologies for electronic materials, energy conversion and storage, and space experiments. Dr. Hepp has been active for ten years in enhancing the involvement of minority students in renewable energy and is a Sequoyah Fellow of the American Indian Science and Engineering Society.

| REPORT DOCUMENTATION PAGE | | | <i>Form Approved</i> <i>OMB No. 0704-0188</i> | |
|---|---|--|--|--|
| Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503. | | | | |
| 1. AGENCY USE ONLY (Leave blank) | | 2. REPORT DATE June 2002 | 3. REPORT TYPE AND DATES COVERED Technical Memorandum | |
| 4. TITLE AND SUBTITLE Single Source Precursors for Thin Film Solar Cells | | | 5. FUNDING NUMBERS WU-755-A4-01-00 | |
| 6. AUTHOR(S) Kulbinder K. Banger, Jennifer A. Hollingsworth, Jerry D. Harris, Jonathan Cowen, William E. Buhro, and Aloysius F. Hepp | | | | |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration John H. Glenn Research Center at Lewis Field Cleveland, Ohio 44135-3191 | | | 8. PERFORMING ORGANIZATION REPORT NUMBER E-13264 | |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Washington, DC 20546-0001 | | | 10. SPONSORING/MONITORING AGENCY REPORT NUMBER NASA TM-2002-211496 | |
| 11. SUPPLEMENTARY NOTES Kulbinder K. Banger, Ohio Aerospace Institute, 22800 Cedar Point Road, Brook Park, Ohio 44142; Jennifer A. Hollingsworth and William E. Buhro, Washington University, Department of Chemistry, One Brookings Drive, St. Louis, Missouri 63130; Jerry D. Harris and Jonathan Cowen, Cleveland State University, Department of Chemistry, Cleveland, Ohio 44115; and Aloysius F. Hepp, NASA Glenn Research Center. Responsible person, Aloysius F. Hepp, organization code 5410, 216-433-3835. | | | | |
| 12a. DISTRIBUTION/AVAILABILITY STATEMENT Unclassified - Unlimited Subject Category: 23 Available electronically at http://gltrs.grc.nasa.gov/GLTRS This publication is available from the NASA Center for AeroSpace Information, 301-621-0390. | | | 12b. DISTRIBUTION CODE | |
| 13. ABSTRACT (Maximum 200 words) The development of thin-film solar cells on flexible, lightweight, space-qualified substrates provides an attractive cost solution to fabricating solar arrays with high specific power, (W/kg). The use of a polycrystalline chalcopyrite absorber layer for thin film solar cells is considered as the next generation photovoltaic devices. At NASA GRC we have focused on the development of new single-source-precursors (SSP) and their utility to deposit the chalcopyrite semi-conducting layer (CIS) onto flexible substrates for solar cell fabrication. The syntheses and thermal modulation of SSP's, via molecular engineering is described. Thin-film fabrication studies demonstrate the SSP's can be used in a spray CVD process, for depositing CIS at reduced temperatures, which display good electrical properties, suitable for PV devices. | | | | |
| 14. SUBJECT TERMS Thin films; Thermoanalysis; Solar cells; Complex compounds | | | 15. NUMBER OF PAGES 30 | |
| | | | 16. PRICE CODE | |
| 17. SECURITY CLASSIFICATION OF REPORT Unclassified | 18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified | 19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified | 20. LIMITATION OF ABSTRACT | |