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Chemical Vapor Deposition for Ultra-Lightweight Thin-Film Solar Arrays for Space

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CHEMICAL VAPOR DEPOSITION FOR ULTRA-LIGHTWEIGHT THIN-FILM SOLAR ARRAYS FOR SPACE

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ABSTRACT

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. A key technical issues outlined in the 2001 U.S. Photovoltaic Roadmap, is the need to develop low cost, high throughput manufacturing for high-efficiency thin film solar cells. At NASA GRC we have focused on the development of new single-source-precursors (SSP's) 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.

INTRODUCTION

One of the key technical issues outlined in the U.S. 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. The National Aeronautics and Space Administration is interested in developing low temperature deposition techniques (Hepp 2001 *et al.*), for producing thin-film photovoltaics. Low temperature routes (<400 °C) allow devices to be deposited onto lightweight polymer substrates such as Kapton™ or polybenzobisoxazole (PBO). These lightweight devices would not only offer cost savings over present technologies, but in many cases would be mission enabling (Hepp 2001, Hoffman 2000 *et al.*, Raffaelle, 2000 *et al.*). One of the most promising family of materials for photovoltaic applications are the chalcopyrite $Cu(Ga,In)(S,Se)_2$ alloys. These materials exhibit high absorption coefficients in the visible to near IR spectrum range, are generally prepared as p-type but can also be prepared n-type by adjusting the stoichiometry of the material, have good electrical characteristics and terrestrial stability, and in the case of $CuInSe_2$, Rockett (1991) *et al.* have demonstrated these to be more radiation tolerant than crystalline silicon and gallium arsenide. Tests on laboratory scale by Ullal (1997) *et al.* show that $CuInSe_2$ based devices have achieved efficiencies approaching 18%. Likewise, Dzionk (1997) *et al.* have shown $CuInS_2$ based devices to achieve conversion efficiencies over 11%, and its direct band gap of 1.5 eV is near optimal for solar radiation utilization. In addition, from an environmental standpoint, $CuInS_2$ is free from the toxicity concerns associated with the selenium analog, and thus may be a more suitable material for terrestrial applications.

To facilitate low temperature deposition, organometallic molecules are used because of their low decomposition temperatures. To avoid premature decomposition of the precursor, atmospheric pressure spray chemical vapor deposition (CVD) was used. Spray CVD combines the benefits of traditional metal-organic chemical vapor deposition (MOCVD) with those of spray pyrolysis, while avoiding the disadvantages of each.

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
$[\{PPh_3\}_2Cu(SEt)_2In(SEt)_2]$ (1)	236	269	25	122	266
$[\{AsPh_3\}_2Cu(SEt)_2In(SEt)_2]$ (2)	205	233	18	47	276
$[\{SbPh_3\}_2Cu(SEt)_2In(SEt)_2]$ (3)	212	239	26	45	271
$[\{PPh_3\}_2Cu(SPr^i)_2In(SPr^i)_2]$ (4)	215	254	29	163	260
$[\{PPh_3\}_2Cu(SPh)_2In(SPh)_2]$ (5)	261	325	22	117	280
$[\{PPh_3\}_2Cu(SePh)_2In(SePh)_2]$ (6)	223	253	22	53	219
$[\{P(Bu^n)_3\}_2Cu(SEt)_2In(SEt)_2]$ (7)	189	238	27	-	264
$[\{P(Bu^n)_3\}_2Cu(S(Pr^n))_2In(SPr^n)_2]$ (8)	171	225	22	-	239

EXPERIMENTAL

All operations of moisture- and air-sensitive materials were performed under an argon atmosphere employing standard Schlenk techniques and a double-manifold vacuum line. Solids were manipulated in an argon filled glovebox. Solvents were freshly distilled from appropriate drying agents under Ar prior to use. The single source precursor, $(PPh_3)_2CuIn(SEt)_4$ was prepared using a procedure reported elsewhere by Hirpo (1993) *et al.*, Hollingsworth (1998) *et al.* and Banger (2001) *et al.* Precursor purity was monitored by nuclear magnetic resonance spectroscopy (NMR) and elemental analysis.

Using a spray CVD reactor similar to Hollingworth's (1999) and Harris (2000) *et al.* 1 μm thick films of $CuInS_2$ were deposited in 70–90 minutes from 150 ml of 0.01 M solution of $(PPh_3)_2CuIn(SEt)_4$ in toluene. The solution was atomized by a 2.5 MHz nebulizer and swept into a two-zone hot-wall reactor by argon carrier gas (4 l/min) that was presaturated with the solvent. Zone one (evaporation zone) of the reactor was held at 128±1 °C, and zone two (deposition zone) was held at 390±1 °C during depositions. For films given a post-deposition anneal at higher temperatures, the carrier gas was reduced to a minimal flow and both zones of the furnace were heated to 600±1 °C in 4 minutes, held isothermal for 8 minutes and then allowed to cool to room temperature.

Films were characterized by transmission spectroscopy (Perkin Elmer, Lambda-19), scanning electron microscopy (SEM) (Hitachi S-3000N), Energy Dispersive Spectroscopy (SEM-EDS) (EDAX), profilometry (KLA-Tencor HRP 75), X-ray diffraction (Philips) and photoelectrochemical analysis. Diode curves were measured for Schottky barriers prepared by thermally evaporating aluminum contacts onto the $CuInS_2$ films. Complete cells with the (top down) composition of $Al/ZnO/CdS/CuInS_2/Mo$/glass were also prepared using the spray CVD deposited films. Films were etched in a 1.5 M KCN solution for one minute, prior to chemical bath deposition of CdS to form the heterojunction. A 1 μm thick layer of fluorine-doped ZnO_2 was sputtered on top of the CdS, followed by thermally evaporated aluminum contacts. Complete cells were characterized under a simulated AM0 solar spectrum.

RESULTS AND DISCUSSION

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* in methanol.

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

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→M, M = Group I Metal)
- 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 (1987), 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. Thus, the use of 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%.

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 $CuInS_2$. Low temperature Differential Scanning Calorimetry (DSC) was used to investigate the liquid phase for **7** and **8** (Figure 1). 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. 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. 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.

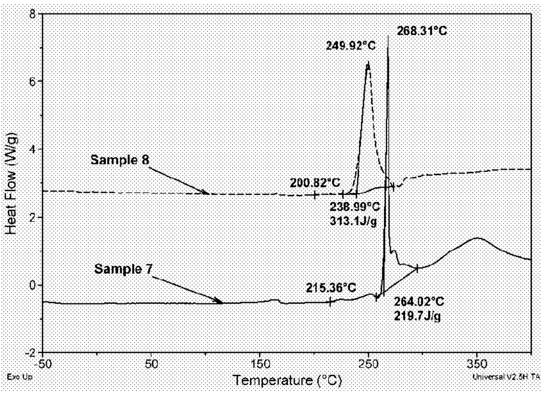

FIGURE 1 LOW TEMP. DSC FOR SSP’s 7 and 8.

Thin-film Study

As deposited, SSP **1** afforded well adhering $CuInS_2$ films, which were dark blue to black, depending on film thickness. (Figure 2). The thickness of a typical film ranged from 0.75 to 1.0 mm, with grain size for the films of less than 0.5 mm As evident from the SEM images, grain growth appears dense and columnar, despite the small grain size (Figure 3). The film thickness varies along the sample, with the thinner portion of the film growing in the "up stream" end of the substrate, and the thick portion of the film growing on the "down stream" end. Thickness uniformity of CVD deposited films has been shown by Rossi *et al.* (1988) to be controlled by the mass transfer rate of species in the gas phase to the substrate surface, and the rate of reaction of the species at the surface. It is believed the observed gradient is a product of temperature inhomogeneities, carrier gas flow rate and incline angle of the substrate holder. Experiments are in progress to minimize variation in film thickness.

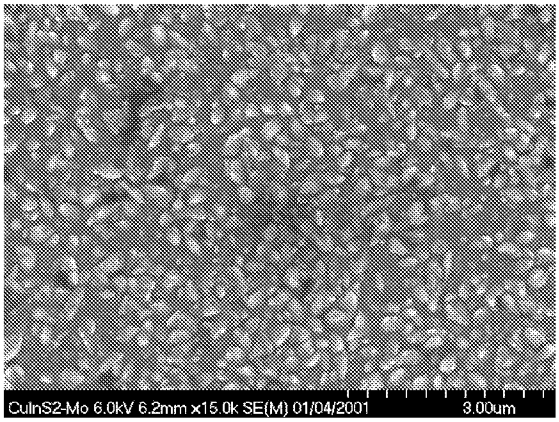

FIGURE 2 SEM OF DEPOSITED CIS FILM USING $[\{P(PPh)_3\}_2Cu(SEt)_2In(SEt)_2]$ **1**.

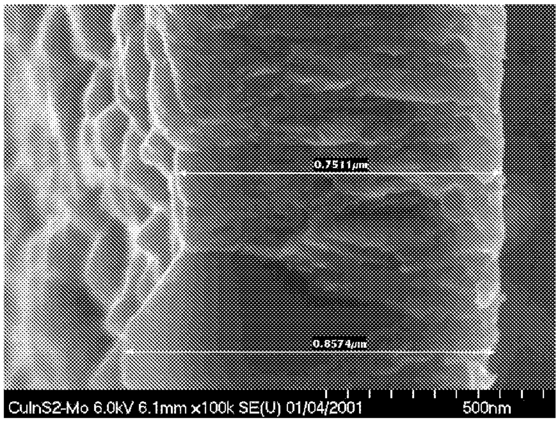

FIGURE 3 SEM EDGE-ON VIEW OF A $CuInS_2$ FILM SHOWING FILM THICKNESS AND COLUMNAR GRAIN GROWTH.

Along with the thickness gradient, there is also a gradient in the crystallographic orientation of the films. As deposited, the majority of a typical film is highly (112) oriented. Over the length of the 76 mm long substrate, the leading 1/3 of the film is (220) oriented, where as the down stream 2/3 of the film are strictly (112) oriented (Figure 4). The observed slight shift in diffraction lines from the front to the back is from the glass substrate warping during annealing causing slight shifts in alignment with the X-ray beam. Siemer (2000) *et al.* have demonstrated that devices prepared from preferred (112) oriented $CuInS_2$ films have better performance than photovoltaic devices fabricated from other oriented films due mainly to a lower series resistance. The reflection at 2Θ = 27° in the front film, labeled with an * has been identified as arising from In_2S_3 and In_2Se_3 in films of $CuInS_2$ and $CuInSe_2$, respectively, prepared by spray pyrolysis. However, spray pyrolyzed films only yield the spurious reflection when indium rich solutions were sprayed. For films grown by spray CVD, the reflection is only observed on the leading 1/3 of the film, yet as will be discussed later, composition of the films remain constant (as determined by SEM-EDS) from front to back. Films deposited by spray CVD also lack the (101) reflection at 2Θ = 17.914°. It is unknown whether this is a product of preferred orientation or lack of long range order since chalcopyrite has the zinc-blend structure with a doubled c-axis and alternating Cu and In atoms replacing the Zn atoms. Using a similar spray CVD reactor, Hollingsworth (1999) demonstrated that crystal orientation is a function of both carrier gas flow rate and solution concentration. It is anticipated that experiments to reduce the thickness gradient will improve the orientation gradient as well, since it is the thinner portion of the film that has the (220) crystal orientation.

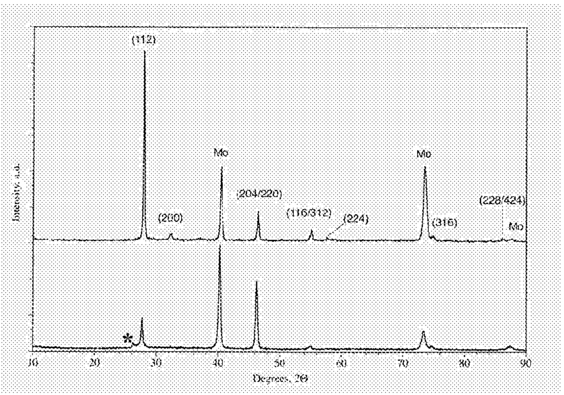

FIGURE 4 X-RAY POWDER DIFFRACTION SPECTRA OF $CuInS_2$ FILM ON MO USING SSP **1**.

Films were deposited onto a variety of substrates, including Ti, Mo and Ni foils, Kapton™, PBO, SiO_2, and Mo coated glass. In all cases, SEM-EDS measurements revealed the films were nearly stoichiometric $CuInS_2$, or only slightly indium and sulfur rich, (with atomic percents for Cu, In and S as 23%, 24% and 53%, respectively). Films deposited on all substrates, except nickel, show no evidence of phosphorous or carbon by SEM-EDS, indicating that the precursor molecules decompose cleanly. Within experimental error of SEM-EDS, the stoichiometry of the films remain constant along their length. SEM-EDS data for films deposited on nickel substrates revealed large quantities of phosphorous (16%) in the material. SEM-EDS measurements of as deposited films on nickel gave atomic percents for Cu, In, S and P as 24%, 17%, 43% and 16%, respectively. Nickel substrates must promote the cracking of the phosphine during deposition, and would thus be unacceptable for device preparation without a passivating layer.

The electrical properties of the films were probed using several techniques. The sheet resistance of several films was measured in the van der Pauw configuration and yielded resistivities ranging from 1 to 30 Ω•cm, which approach values obtained from multi-source sputtered $CuInS_2$ by Scheer (1997) *et al.* These resistivities are also lower than those previously obtained for $CuInS_2$ films deposited using the same single source precursor by Hollingsworth (1999).

To further evaluate the electrical properties of the deposited films, current verses voltage (IV) measurements were recorded for the films using thermally evaporated aluminum point contacts (10 mm^2) to make Schottky barrier diodes. Many of the Schottky barriers were excellent diodes on films annealed at 600 °C, with "turn on" voltages of 0.6–0.8 volts and little leakage when reverse biased. However, many of the contacts on the as-deposited films gave large reverse bias currents and nearly ohmic response (Figure 5). 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, as considerable narrowing of the diffraction lines was observed in the annealed films.

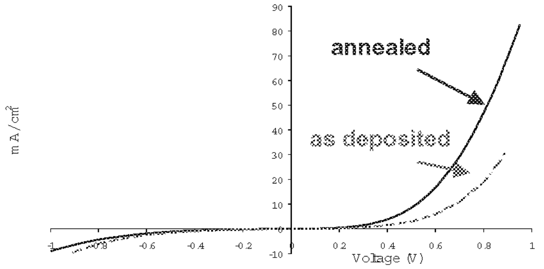

FIGURE 5 SCHOTTKY BARRIER MADE FROM EVAPORATED AL ON $CuInS_2$ ON MO FOIL USING SSP 1.

Complete solar cells were prepared from annealed films deposited on Mo coated glass substrates. The 10 mm × 76 mm cell was mechanically scribed into many smaller cells, with an IV curve for each measured under a simulated AM0 light source. The maximum efficiency achieved by one of the small area cells was 0.68% (Figure 6), which was located approximately midway along the 76 cm substrate and had a total area of 0.5 cm^2. The most obvious feature of the IV curve is the lack of a "knee," given that the curve is nearly linear. From the slope of the curve near the open circuit voltage (Voc), the device appears to have high series resistance. At this time it is unknown whether the series resistance is from the absorber layer, from the interfaces between the different layers or both. For an ideal diode, the curve would intersect normal to the y-axis. From the slope of the line near the short circuit current (Isc), the film also has high shunt resistance. The mechanical scribing of the small area cells could have caused the shunting.

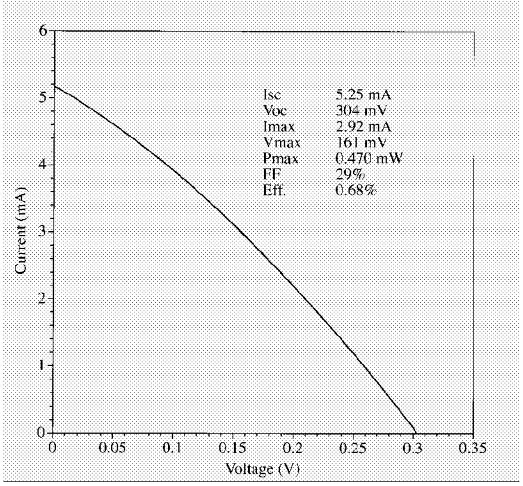

FIGURE 6 CURRENT-VOLTAGE CURVE FOR A 0.5 CM^2 $CuInS_2$ CELL ON Mo COATED GLASS.

SUMMARY AND OUTLOOK

Working photovoltaic devices have been prepared from atmospheric pressure spray CVD deposited $CuInS_2$ thin films using the single source precursor $(PPh_3)_2CuIn(SEt)_4$. Although the Voc, Isc and fill factor are low, it is anticipated that these will increase as deposition parameters are optimized. X-ray diffraction of the films reveal there is a preferred orientation gradient along the substrate, with only the back two thirds of the film having the desired (112) crystal orientation. The films also range in thickness, with the leading edge being thinner than the trailing edge. Spray CVD is a promising technique for depositing $CuInS_2$ on to low temperature substrates such as Kapton™ and PBO at temperatures below 400 °C. However, the films with the best electrical properties were annealed at 600 °C following deposition at 390 °C. The versatility of the $[\{LR_3\}_2Cu(ER')_2M(ER')_2]$ 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 $CuGaE_2$ (E= S, Se) thin-films on flexible polymer substrates at reduced temperatures. Although tests for the deposition of the wide bandgap alloy $Cu(Ga{:}In)S_2$, 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-VI_2 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 are 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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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. A key technical issues outlined in the 2001 U.S. Photovoltaic Roadmap, is the need to develop low cost, high throughput manufacturing for high-efficiency thin film solar cells. At NASA GRC we have focused on the development of new single-source-precursors (SSPs) and their utility to deposit the chalcopyrite semi-conducting layer (CIS) onto flexible substrates for solar cell fabrication. The syntheses and thermal modulation of SSPs via molecular engineering is described. Thin-film fabrication studies demonstrate the SSPs 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

Solar cells; Indium compounds; Copper compounds; Thin films; Vapor deposition

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