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SYNTHESIS AND CHARACTERIZATION OF $CuInS_2$ SINGLE SOURCE PRECURSORS FOR CHEMICAL VAPOR DEPOSITION

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Abstract

A family of single source precursors, for the spray chemical vapor deposition (CVD) of chalcopyrite thin films ($CuInS_2$), has been synthesized in good yields (ca. 65%). Newly synthesized compounds include $[\{L\}_2Cu(SR)_2In(SR)_2]$, ($R$=alkyl, aryl; L=neutral donor ligand). The use of the single source precursors provides an attractive alternative over conventionally used multi-source precursors, which are often toxic, air sensitive and pyrophoric. However, it is desirable that these thin films be processed on flexible polymer substrates such as Kapton^{TM}. Therefore, milder deposition temperatures are needed to maintain the structural integrity of the underlying polymer substrates. By selective manipulation of the steric and electronic properties of the precursor, milder processing temperatures may be employed, while mainting the desired stoichiometry of the deposited films. Elucidation of the structures have been confirmed by the use of NMR. Thermal analytical techniques, differential scanning calorimetry (DSC) and thermogravimetric analysis (TG), have been employed to determine thermal profiles of each candidate compound.

Keywords: DSC, NMR, precursors, TG, thin films

Introduction

Photovoltaic devices, which incorporate the use of $CuInS_2$ as the absorber layer of the cell, have been reported with efficiencies as high as 11.4% [1]. The use of chalcopyrite absorbers are highly appealing since their bandgaps correlate well for their use in terrestrial (AM 1.5) and space (AM 0) applications.

Additionally, $CuInS_2$ based solar cells have been found to be among the most radiation resistant. However, for space applications it is desirable that these solar cells be fabricated on flexible substrates such as Kapton^{TM} (a space qualified polyimide). With the incorporation of flexible substrates higher packing efficiencies can be achieved

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when deploying arrays into orbit. Although current efficiencies for thin-film solar cells are less than rigid silicon arrays, there is an order of magnitude increase in the specific power (W kg^{-1}). The fact that the $CuInS_2$ based cells are radiation tolerant and yield a high specific power renders them a viable prospect for space applications. With an estimated launch cost of \$11 K kg^{-1} for a low-earth orbit satellite and \$66 K kg^{-1} for a geosynchronous earth orbit satellite, a significant decrease in the mass of an array will significantly reduce launch costs [2].

Current methods employed for processing thin-film $CuInS_2$ devises require techniques such as co-evaporation of the elements, which involve high temperature sulphurization steps [1]. Low temperature (<400°C) deposition processes are needed to incorporate flexible polymer substrates. A major advancement in improving the processing of these types of solar arrays is the use of chemical vapor deposition (CVD). The fundamental steps include: vaporization and transport of the precursor into the reactor; diffusion of the precursor to the substrate; decomposition of the precursor; formation of $CuInS_2$; recombination of the by products and desorption into the gas phase. A more detailed description of a spray CVD reactor is given elsewhere [3, 4]. While deposition parameters must be optimized to compete with cell efficiencies reported by more conventional processes, the use of single source precursors provides an attractive alternative over more complex multi-step deposition processes.

Recently we have been engaged into looking for milder processing routes via single source precursor CVD. The use of chalcopyrite tertiary single source precursors afford such a processes. A family of single source precursors has been synthesized with the I-III-VI_2 stoichiometry built in [5]. Newly synthesized compound include $[\{L\}_2Cu(SR)_2In(SR)_2]$, ($R$=alkyl, aryl; L=neutral donor ligand).

Experimental

The compounds are synthesized based on modification of the procedure reported by Kanatzidis [6], with the exception of the thiolato anion being generated in situ by the reaction of the conjugate acid with NaOMe in methanol. All reactions were carried out under an inert atmosphere.

The candidate structures have been confirmed with the use of a 300 MHz Bruker NMR. A TA 950 thermogravimetric analyzer and a 910 differential scanning calorimeter were used to thermally profile each compound. Evolved gas analysis (EGA) was performed by a TA 1950 TGA coupled to a Perkin Elmer FTIR spectrophotometer and a thermal quest mass spectrometer (EI). The TG and DSC were heated at 10° min^{-1} in a dinitrogen flow of 50 mL min^{-1}.

Deposited films were characterized by scanning electron microscopy (SEM) (Hitachi S-3000N), energy dispersive spectroscopy (EDS), (EDAX) and X-ray diffraction (Phillips PW3710) (CuK_α, 1.541 Å). Current *vs.* voltage measurements were performed by a Keithley 236 source measure unit.

Results and discussion

NMR, DSC and TG with EGA were used to characterize and verify precursor formation and purity. Proton NMR spectra confirmed the correct stoichiometry of organic functional groups present in the analogs under investigation as well as the absence of any starting materials. Data derived from TG revealed the onset temperatures, the temperature corresponding to the point maximum rate of mass loss (MRW), and the percent of non-volatile residue ($CuInS_2$). Two main thermal events are of importance on the DSC plots, an endothermal event assignable to the melting point of a solid precursor and an exothermal event assignable to the decomposition of the precursor. Table 1 represents the compounds under investigation as well as a summary of the thermal data acquired from the DSC and TG thermal profiles. Decomposition temperatures, listed in the last column of Table 1, display a range of temperatures in which the precursors decompose from 239°C for **7** and 280°C for **5**. Additionally the temperature corresponding to the MRW ranges from 225°C for **7** and 325°C for **5**. These temperature ranges demonstrate the ability to modify the chemical and physical properties of these precursors.

Altering the Lewis acid-base interaction between the donor ligand and the Cu changes the overall stability of the molecule. Hence, the Drago–Wayland approximation can be used for ternary single source precursor design, to quantitatively estimate the strength of the Lewis acid-base interaction between the copper center and the neutral donor [7]. The cleavage of the chalcogenide (R-group) also plays a significant role in the thermal stability. A more sterically demanding R-group provides a better leaving ability for the chalcogenide.

Table 1 Thermal data acquired from the DSC and TG thermal profiles

Single source precursors	TG			DSC	
	Onset/ °C	Temperature/°C MRW	Residue/ %	M. P.	Decomp./ °C
1 $[\{PPh_3\}_2Cu(SEt)_2In(SEt)_2]$	237	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 $[\{P(Bu^n)_3\}_2Cu(SEt)_2In(SEt)_2]$	189	238	27	–	264
7 $[\{P(Bu^n)_3\}_2Cu(SPr^n)_2In(SPr^n)_2]$	171	225	22	–	239

The extrapolated onset for $[\{PPh_3\}_2Cu(SEt)_2In(SEt)_2]$, (**1**), is found to be 237°C, with a temperature corresponding to a MRW at 269°C, and a residue of 25.49% (Fig. 1). Based on the residue of 25.49%, the efficiency of the precursor to afford $CuInS_2$ is found to be within 0.1%. The following reactions represent the breakdown of the single source precursor (SSP) to yield $CuInS_2$.

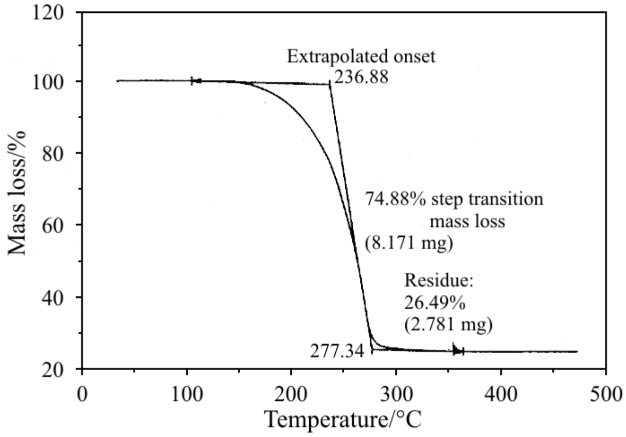

Fig. 1 TG plot of $[\{PPh_3\}_2Cu(SEt)_2In(SEt)_2]$

$$SSP \rightarrow 2L + 2SR + CuInS_2$$

DSC of the same compound, (I), reveals complimentary thermal data. From the DSC, the melting point is found to be 122°C and the decomposition temperature to be 266°C. Information provided by the TG and DSC plots not only demonstrate that the precursors breakdown cleanly to yield $CuInS_2$, but more importantly the temperatures at which the precursors decompose and organic by products volatilize. This information is crucial for determining the parameters of the CVD reactor (i.e. substrate temperature setting). In low temperature DSC experiments, using controlled cooling, both samples 6 and **7** were found not to show an endotherm assignable to a melting phase transition (Fig. 2). Compounds 6 and 7 represent the first liquid single source precursors for the CVD of $CuInS_2$.

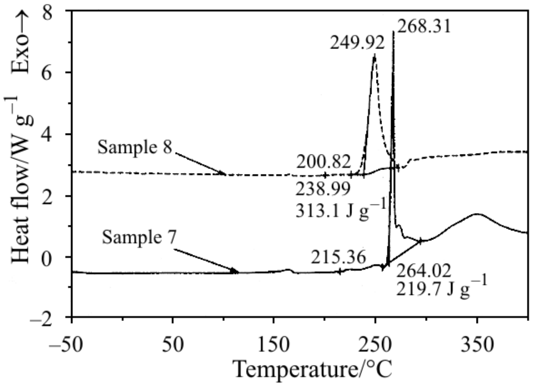

Fig. 2 Low temperature DSC for $[\{P(Bu^n)_3\}_2Cu(SEt)_2In(SEt)_2]$ and $[\{P(Bu^n)_3\}_2Cu(S(Pr^n))_2In(SPr^n)_2]$

To verify the mechanism of decomposition for the precursors, EGA via FTIR and mass spectrometry was investigated. The FTIR spectra for 6 (Fig. 3), show absorptions at approx. 3000, 1460, 1390, 1300 and 1250 cm^{-1}, which are assignable to the initial expulsion of diethyl sulphide.

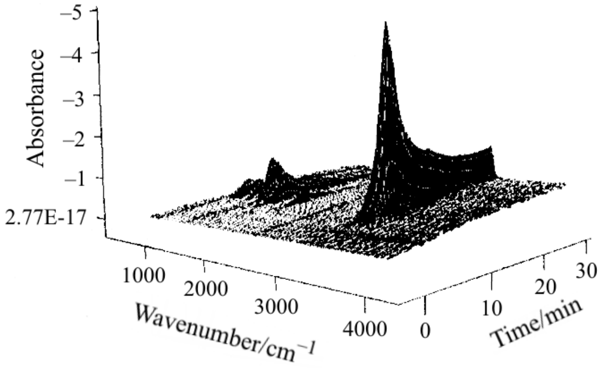

Fig. 3 EGA-FTIR spectra for $[\{P(n\text{-}Bu)_3\}_2Cu(SEt)_2In(SEt)_2]$ **6**

Correlation with the mass spectra supports these findings on the basis of the library fit and from the assignment of the fragment and parent ions, (*m*/*z* 90). Comparison with the respective mass spectra (Fig. 4), allows for the assignment to the loss of PBu_3, with a library fit of 92% and assignment of the parent ion (*m*/*z*=202). Importantly, mass spectroscopic EGA shows the absence of any fragment ions with an isotopic pattern associated with an indium derivative. In similar experiments, EGA for the *n*-propyl derivative gave analogous results, however for 1–5, EGA was only able

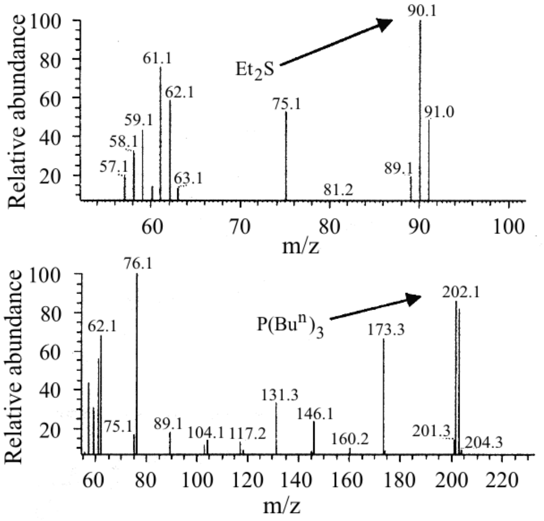

Fig. 4 EGA: mass spec data from TG for $[\{P(n\text{-}Bu)_3\}_2Cu(SEt)_2In(SEt)_2]$, **6**

to confirm the extrusion of the dialkylsulphide. The inability to detect the group V donors may be attributed to their lower volatile.

The ability of the new precursors to thermally decompose to yield single-phase CIS was investigated by powder XRD analysis and EDS on the non-volatile solids from the TG experiments of selective compounds. XRD spectra for the non-volatile material produced from the pyrolysis of 6 with the JCPDS reference patterns for $CuInS_2$ (27-0159), confirmed it to be single-phase $CuInS_2$ (Fig. 5).

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 6 and 28, 23 and 49 for 7, respectively, thus supporting the formation of $CuInS_2$.

Electronic properties of the deposited thin films were evaluated by performing current *vs*. voltage measurements (Fig. 6). Approximately 1 μm thick films were deposited onto molybdenum foil. Aluminum contacts (~40 μm thick) were deposited on top of $CuInS_2$ to make Schottky barrier diodes. Diode characteristics were found to significantly improve after annealing deposited films at 375°C for 1 h under flowing argon.

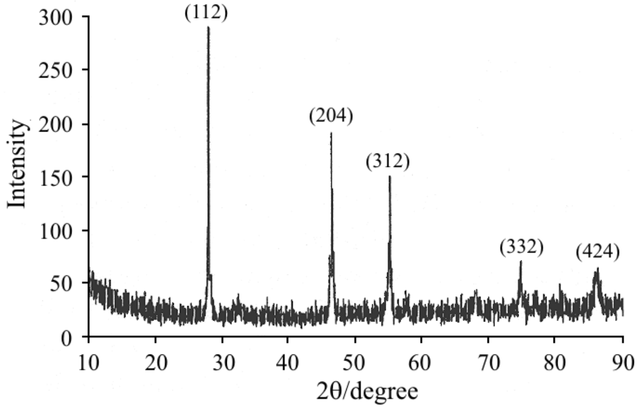

Fig. 5 XRD powder diffraciton for non-volatile residue from pyrolysis of $[\{P(n\text{-}Bu)_3\}_2Cu(SEt)_2In(SEt)_2]$, ($CuK_\alpha$, 1.541 Å)

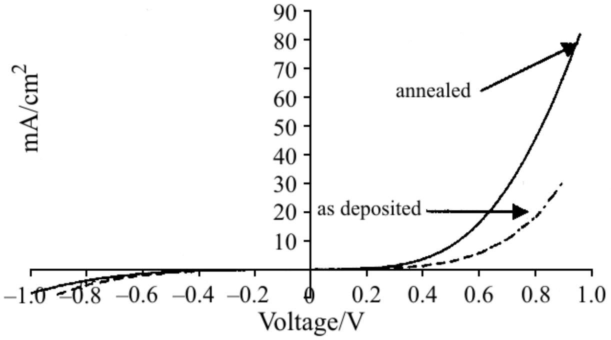

Fig. 6 Current density *vs.* voltage plot of Schottky barrier diodes

Conclusions

It has been demonstrated that by the manipulation of the neutral donor ligand to the copper center and alteration of the functional groups present on the chalcogenide, one can substantially alter the decomposition temperatures of the single source precursor. Thermal analysis methods, TG, TG-EGA and DSC, provide essential data for the application of single source precursors to spray CVD. Additionally, EGA via mass spectrometry reveals that the precursors decompose by the loss of the sulphide group followed by the loss of the neutral donor. XRD patterns of the pyrolyzed material confirm the formation of single phase polycrystalline $CuInS_2$.

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