Synthesis, Characterization and Decomposition Studies of Tris(N,N-dibenzyldithiocarbamato) Indium(III): Chemical Spray Deposition of Polycrystalline CuInS$_2$ on Copper Films

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Tris(bis(phenylmethyl)carbamodithioato-S,S'), commonly referred to as tris(N,N-dibenzyldithiocarbamato)indium(III), In(S$_2$CNBz$_2$)$_3$, was synthesized and characterized by single crystal X-ray crystallography. The compound crystallizes in the triclinic space group P$\bar{1}$ with two molecules per unit cell. The material was further characterized using a novel analytical system employing the combined powers of thermogravimetric analysis, gas chromatography/mass spectrometry and Fourier-Transform infrared spectroscopy to investigate its potential use as a precursor for the chemical vapor deposition (CVD) of thin film materials for photovoltaic applications. Upon heating, the material thermally decomposes to release CS$_2$ and benzyl moieties in to the gas phase, resulting in bulk In$_2$S$_3$. Preliminary spray CVD experiments indicate that In(S$_2$CNBz$_2$)$_3$ decomposed on a Cu substrate reacts to produce stoichiometric CuInS$_2$ films.

1. Introduction

As the technology of satellites and space vehicles continues to advance, the demands for lower cost photovoltaic arrays to power on-board instruments intensifies. Although power requirements are mission specific, technologies which promise high mass specific power (W/kg) are desirable since they would translate into lower overall mission costs. While crystalline silicon, gallium arsenide, and related multijunction III-V cells offer high efficiencies, they are costly. Alternatively, polycrystalline thin film materials are appealing for applications in space photovoltaic devices in view of their 1) high radiation

resistance, 2) ability to be deposited in thin layers on flexible light weight substrates, and 3) lower overall material and production costs (ref. 1). The possible integration of thin film materials into tandem or multijuction cells offers another promising alternative to achieving higher efficiency cells at a lower overall cost (ref. 2).

An assessment of thin film solar cell technology indicates that a cell efficiency of ~12 percent is required to match the mass specific power (performance) of an array utilizing crystalline cell technology (ref. 3). Two potential candidates are poly-crystalline copper indium disulfide ($CuInS_2$) and copper indium diselenide ($CuInSe_2$) thin films. While both materials offer advantages over crystalline thin film technology, processing of $CuInS_2$ is more attractive than $CuInSe_2$ since potential material hazards are not as severe in the former case (ref. 4). Additionally, $CuInS_2$ has a bulk bandgap of 1.5eV, which is near optimal for harvesting solar radiation (refs. 4 to 6). Cells with efficiencies up to 11.4 percent have been demonstrated and encourage further investigation of this material (ref. 6).

The integration of photovoltaic devices onto flexible substrates requires that device fabrication be achieved at temperatures below the melting point, decomposition temperature or transition temperature of the substrates (i.e., 385 °C for Kapton (ref. 7) or 550 °C for polyphenylenebenzobisoxazole (PBO) (ref. 8)). Current techniques require a high temperature post-deposition treatment in order to obtain the crystal quality necessary for high performance films (ref. 6). In this respect, our group has been studying compounds that are promising molecular precursors for low temperature (<400 °C) chemical vapor deposition of $CuInS_2$ based polycrystalline thin films (refs. 9 to 12).

One potential group of precursors for the deposition of these materials is dithiocarbamates. In addition to being relatively simple to synthesize and easy to handle, these compounds are expected to undergo simple and clean decomposition, making them ideal for CVD applications. Tris(dibenzyldithiocarbamato)indium(III) was selected for assessment because of its bonding configuration and its anticipated decomposition characteristics, and was expected to yield pure indium sulfide.

2. Experimental Techniques and Methods of Analysis

2.1 Synthesis of Tris(dibenzyldithio-carbamato)indium(III)

Dibenzyldithiocarbamic acid, sodium salt (9.48g, 32 mmol) (Sigma-Aldrich Inc.) was dissolved in approximately 50 mL of methanol (Pharmco Products Inc.). The dissolved ligand salt was added dropwise to a solution of indium trichloride (2.37 g, 10.7 mmol) (Sigma-Aldrich Inc.) dissolved in 16 mL of 75/25 percent methanol/distilled water. A white precipitate formed with the addition of the ligand salt, and the mixture was allowed to stir for approximately 22 hours. The mixture was vacuum filtered and allowed to air dry. Yield: 11.02 g of crude white product. The crude product (11.02 g) was slurried in approximately 170 mL of dichloromethane (Sigma-Aldrich Inc.). The resulting solution was vacuum filtered, and the volume of the filtrate was doubled with the addition of hexanes (Fisher Scientific HPLC grade). The volume of the filtrate was reduced by 2/3 under vacuum; the resulting solid was separated by vacuum filtration and washed twice with hexanes. The white product was allowed to air dry. Yield: 9.04 g, 81.2 percent. Found: C, 57.55; H, 4.57; N, 4.38 percent. Calc. for $In(S_2CNBz_2)_3$: C, 57.98; H, 4.54; N, 4.51 percent.

2.2 Single-Crystal X-ray Crystallography

Single crystals of tris(N,N-dibenzyldithiocarbamato)indium(III) ($In(S_2CNBz_2)_3$, (Compound 1) were grown at room temperature by layering a concentrated dichloromethane solution of the product with hexanes. Hexanes slowly diffused into the dichloromethane solution and single crystals of the product grew in the mixed solvent solution. A colorless plate shaped crystal was mounted onto a glass fiber in a random orientation. Data were collected at 150 K using a Nonius KappaCCD diffractometer. A

hemisphere of data was collected to a maximum 2θ of 55.0°. Relevant crystallographic data are summarized in table 1.

The structure was solved by direct methods using SIR97 (ref. 13). The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were placed in calculated positions according to idealized geometries. They were included in the refinement, but restrained to ride on the atom to which they were bonded. An empirical absorption correction using SCALEPACK was applied (ref.14) The structure was refined in full-matrix least-squares, where the function minimized was $\Sigma w(\mid F_o \mid^2 - \mid F_c \mid^2)^2$ and the weighting factor w was of the form $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$, where $P = (F_o^2 + 2F_c^2)/3$. The final refinements were performed using the program SHELXL-97 (ref. 15). All non-hydrogen atoms were refined with anisotropic thermal parameters. The largest remaining peak in the final difference map was 0.44 e/Å^2.

2.3 Thermal Characterization

Thermal decomposition experiments were carried out in situ using a multi-analytical tool equipped to provide analytical information on the decomposition behavior of a compound as a function of time and temperature. This fully integrated system, known as a precursor analysis and characterization cluster tool (PACT, see ref. 11), allows real time characterization of the gaseous species evolved as a substance undergoes thermal decomposition. The system consists of a Cahn TG-2131 thermogravimetric analysis (TGA) unit interfaced to a ThermoQuest GCQ plus gas chromatography-mass spectrometer (GC-MS) and a Nicolet 750 Magna-IR Fourier transform infrared (FTIR) spectrometer. The mass spectrometer may be used to separate exhaust gas mixtures via the GC or may be used to perform real-time evolved gas analysis through direct injection of the TGA gases into the mass spectrometer.

Samples of $In(S_2CNBz_2)_3$ (35–40 mg) were loaded into the TGA, and the chamber was purged with helium (130 slpm) for one hour prior to heating. Samples were heated from 30 to 650 °C at a rate of 5 °C/minute. During heat treatment, gaseous by-products were drawn into the GC/MS and FTIR for analysis. The gas chromatograph consists of a Restek RTX-5MS column (30 m × 0.25 μm). The mass spectrometer was operated using 70 eV electron energy in electron impact mode. The FTIR spectrum was measured in the range of 4000 cm^{-1} to 650 cm^{-1} using a potassium bromide beamsplitter and a mercury cadmium telluride detector.

Mass spectral data were compared to reference spectra in the National Institute of Standard and Technology database and to spectra obtained from authentic samples where possible. IR data were compared to reference spectra in the Aldrich Vapor Phase Sample and the Aldrich Condensed Phase Sample libraries. Residual solids (powders) were characterized by X-ray diffraction (XRD), and the data were compared to XRD data in the Joint Committee for Powder Diffraction Standards (JCPDS) library.

2.4 Film Deposition

Using an atmospheric pressure spray CVD reactor, (refs. 10 to 12, and 16 to19) films of In_2S_3 were deposited from toluene solutions (0.005–0.01 M) of $In(S_2CNBz_2)_3$ onto glass and titanium; argon carrier gas flow rates were kept between 2 and 4 slm. In_2S_3 was also deposited onto Cu-coated glass and Cu-coated Ti substrates to produce $CuInS_2$ films; Cu films were deposited by thermal evaporation. Solutions were atomized by a 2.5 MHz nebulizer and swept into a two-zone hot-wall reactor by argon carrier gas (2–4 slpm) that was presaturated with the solvent. The two zone atmospheric spray CVD system used for film growth experiments were described earlier (refs. 9 to 12). Zone one (evaporation zone) of the reactor was held at 130 °C, and zone two (deposition zone and substrate temperatures) ranged from 325 to 450 °C. $CuInS_2$ films were grown on copper (Cu) on glass and copper on (Ti) substrates. Films were cooled under reduced argon flow rates (500 sccm).

3. Results and Discussion

3.1 X-ray Structural Characterization of In(S$_2$CNBz$_2$)$_3$

The title compound was synthesized in good yield by reacting InCl$_3$ with a stoichiometric amount of the dithiocarbamate ligand salt. The white product was found to be insoluble in water and alcohols, sparingly soluble in acetone, and soluble in dichloromethane, chloroform, and toluene.

The triclinic unit cell of the title compound contains two molecules of In(S$_2$CNBz$_2$)$_3$. The product is composed of three bidentate dibenzyldithiocarbamate ligands bound to an In^{3+} ion (fig. 1). The small bite angle of the ligands gives the molecule a distorted octahedral geometry. Intraligand S–In–S bond angles range from 69.465(18) to 70.412(17)°, while interligand S–In–S bond angles range from 92.236 to 104.272(19)° (table 2). The S–C–S angles of the ligands are within three standard deviations (3σ of each other with an average bond angle of 118.6°. Metal–sulfur bond distances range from 2.5750(6) Å to 2.6189(6) Å. All carbon–sulfur bond distances, with the exception of C(3)–S(32) which is just outside the range, are within 3σ of the average C–S bond distance of 1.727 Å, indicating electron delocalization within the CS$_2$ network. Carbon–nitrogen bonds are consistent with electron delocalization within the ligands. The average C–N bond distance of 1.329 Å is considerable shorter than a normal carbon–nitrogen single bond, indicating some double bond character. Electron delocalization is also supported by IR spectroscopy data. A single band at 1027 cm^{-1} is attributed to ν(S–C), indicative of bidentate binding. The band attributed to ν(C–N) is at 1493 cm^{-1}, and is again consistent with a partial double bond (ref. 20). In general, the overall geometry and metrics of the molecule resemble those of the other reported tris(dithiocarbamato)indium(III) complexes (refs. 20 to 24).

3.2 Thermal Characterization of In(S$_2$CNBz$_2$)$_3$

Initial thermal experiments found In(S$_2$CNBz$_2$)$_3$ to decompose in the range of 185 to 205 °C; the material was characterized using our integrated analysis tool or PACT. The PACT integrates a TGA with both GC/MS and FTIR providing complementary information on gaseous decomposition chemistry. This analytical cluster tool configuration provides the unique ability to investigate the decomposition behavior of promising CVD precursor materials.

Thermal decomposition of In(S$_2$CNBz$_2$)$_3$ was investigated; a typical TGA plot of In(S$_2$CNBz$_2$)$_3$ is given in figure 2. The data indicated a single sharp weight loss occurring with an onset temperature of 328 °C, although a color change to dark orange was noted at 270 °C. Continued heating to 600 °C resulted in a total weight loss of 82.2 percent. This information in conjunction with EDAX analysis of the residue indicated formation of pure In$_2$S$_3$. Direct analysis of the gases as evolved during decomposition by MS (fig. 3) and FTIR (fig. 4) indicate that while decomposition appears to proceed in one step from the TGA, in fact it must be a multi-step process.

By looking specifically at the m/e 76 ion (fig. 5a) in the mass spectrum as a function of time, it can be seen that this ion reaches a maximum intensity at 16 minutes drops off and again rises to a relative maximum at 20.5 minutes. The FTIR and Mass spectra corresponding to a time of 16 minutes (fig. 6a and inset, respectively) are virtually identical to those of pure CS$_2$ by comparison to known spectra. Looking at the FTIR spectrum taken at 18 minutes (fig. 6b) shows peaks occurring near 2950 cm^{-1} are attributed to alkyl group bonding present in the benzyl portion of the parent ligand. Looking at the mass spectrum corresponding to 18 minutes (fig. 6b inset), characteristic peaks of the benzyl group can be seen, 91 and 92 m/e but higher molecular weight peaks are also present, see figure 5b for m/e = 91 profile. At higher temperatures, the spectra become complex showing characteristic C–S, C–N, and C = N vibrations. By mass spectral comparison, it is probable that both benzyl thiocyanate is produced as one product during

later stages of decomposition. The combined MS and FTIR data (figs. 3 to 6) indicate that the first group to evolve from the precursor molecule is carbon disulfide followed by loss of the benzyl group.

The residual powder obtained following thermal decomposition was characterized by scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) and powder X-ray diffraction (XRD). EDS data for the material revealed a composition (within experimental error) of In_2S_3. Figure 7 presents an XRD pattern of the final product that resulted from the heat treatment of an $In(S_2CNBz_2)_3$ sample. The major diffraction peak occurs at a 2θ value of $47.7°$ with a FWHM value of $0.7°$. Comparison with the Joint Committee for Powder Diffraction Standards data (JCPDS # 73–1366) indicates that the final product is body-centered tetragonal β-In_2S_3. These results indicate that $In(S_2CNBz_2)_3$ follows a thermal decomposition pathway that produces stoichiometric In_2S_3 films.

3.3 Spray CVD of In_2S_3 and $CuInS_2$ Films

Using the results from the PACT as a guide, films of In_2S_3 were deposited using a two-zone, hot-wall, atmospheric pressure spray CVD reactor. The advantages of spray CVD over conventional CVD are that the need for vacuum technology is eliminated, and the use of precursor materials with low volatility is not a limiting factor.

In general, experiments that were performed using high flow rates (4 slm) and/or high precursor concentrations (0.01 M) had a greater tendency to result in powders. Lower flow rates (2 slpm) and lower concentrations (0.005 M) tended to yield films. Appreciable film deposition did not occur until 375 °C. EDS analysis showed that films deposited on bare Ti or glass substrates yielded pure In_2S_3 at this temperature. EDS data indicated that nearly stoichiometric $CuInS_2$ films were achieved by utilizing Cu on Ti substrates. This implies that it may not be necessary to use a precursor solution containing both In and Cu compounds. Film stoichiometry can be modified by adjusting the thickness of the Cu layer on the substrate. Figure 8 exhibits a scanning electron micrograph of a film deposited on Cu/Ti at 425 °C, using a 0.005 M solution and 2 slm Ar carrier gas and shows aggregations of small grains on the surface of the $CuInS_2$ films. This figure is representative of the film morphology observed in these experiments. It was apparent that although cluster size increased with increasing substrate temperature, there appeared to be little change in surface grain size with respect to substrate temperature. XRD analysis of these films confirmed that these films have the chalcopyrite structure (see fig. 9). Unlabeled peaks in the XRD pattern are attributed to the underlying Ti substrate.

4. Conclusions

This paper presents the systematic synthesis and characterization of $In(S_2CNBz_2)_3$, and its potential use as a precursor for the chemical vapor deposition of In_2S_3 thin films for thin film photovoltaic applications. The material was characterized The material was characterized by single crystal X-ray diffraction and its thermal properties were probed using a specialized tool employing the combined analytical techniques of thermogravimetric analysis, gas chromatography/mass spectrometry and Fourier-Transform infrared spectroscopy. Examination of the gas phase species produced during heating, and evaluation of the composition and structure of the resulting solids confirm that this precursor can be used to deposit pure indium sulfide. Implementation of $In(S_2CNBz_2)_3$ in a spray CVD apparatus indicates that it is possible to achieve pure In_2S_3 films with this precursor. However, further investigations are warranted to determine the feasibility of achieving device quality $CuInS_2$ films.

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TABLE 1. — CRYSTALLOGRAPHIC DATA FORTRIS(BIS(PHENYLMETHYL)
CARBAMODITHIOATO-S,S')INDIUM (III)

Molecular formula	$C_{45}H_{42}InN_3S_6$
Formula weight	932.06
Temperature (K)	150
Radiation (wavelength)	Mo K_α(0.71073Å)
Space group	P $\bar{1}$ (No. 2)
a (Å)	9.9396(2)
b (Å)	12.9719(3)
c (Å)	16.7988(4)
α (°)	91.9439(8)
β (°)	97.6047(8)
γ (°)	103.2196(13)
V, (Å^3)	2085.39(8)
Z	2
D_{calc} (g cm^{-3})	1.484
Crystal size, mm	0.44×0.40×0.25
μ (mm^{-1})	0.881
h, k, l range	0 to 12,–16 to 16,–21 to 21
2θ range (°)	2.45 to 54.95
Data collected	19459
Unique data	9255
Data used in refinement	9220
Cutoff used in R-factor calculations	$F_o^2 > 2.0\sigma(F_o^2)$
Data with I > 2.0σ(I)	7423
Parameters	496
$R(F_o)$	0.033
$R_w(F_o^2)$	0.072
Goodness-of-fit	1.042

TABLE 2. — SELECTED BOND DISTANCES AND ANGLES FOR COMPOUND 1, In(S$_2$CNBz$_2$)$_3$

In–S(11)	2.5887(6)	S(11)–In–S(12)	69.465(18)
In–S(12)	2.6189(6)	S(21)–In–S(22)	69.654(17)
In–S(21)	2.5750(6)	S(32)–In–S(31)	70.412(17)
In–S(22)	2.6170(6)	S(11)–In–S(21)	92.718(18)
In–S(31)	2.5941(6)	S(11)–In–S(31)	94.76(2)
In–S(32)	2.5669(6)	S(11)–In–S(32)	104.272(19)
S(11)–C(1)	1.723(2)	S(22)–In–S(12)	97.593(19)
S(12)–C(1)	1.732(2)	S(22)–In–S(31)	100.03(2)
S(21)–C(2)	1.726(2)	S(22)–In–S(32)	95.804(18)
S(22)–C(2)	1.722(2)	S(21)–In–S(31)	97.289(19)
S(31)–C(3)	1.721(2)	S(21)–In–S(12)	92.236(19)
S(32)–C(3)	1.736(2)	S(12)–In–S(32)	104.221(18)
N(1)–C(1)	1.328(3)	S(11)–In–S(22)	158.18(2)
N(1)–C(120)	1.470(3)	S(21)–In–S(32)	159.56(2)
N(1)–C(110)	1.475(3)	S(12)–In–S(31)	162.00(2)
N(2)–C(2)	1.332(3)	S(11)–C(1)–S(12)	118.38(13)
N(2)–C(210)	1.477(3)	S(21)–C(2)–S(22)	118.64(13)
N(2)–C(220)	1.480(3)	S(31)–C(3)–S(32)	118.78(13)
N(3)–C(3)	1.328(3)		
N(3)–C(320)	1.473(3)		
N(3)–C(310)	1.486(2)		

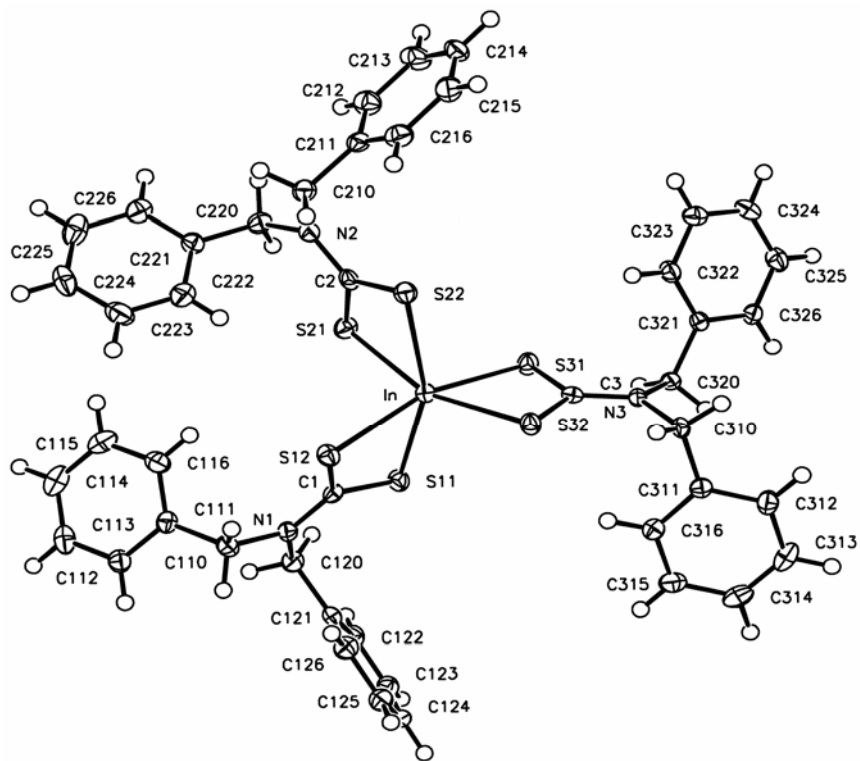Numbers in parentheses are estimated standard deviations in the least significant digits.

Figure 1.—ORTEP diagram of tris(N,N-dibenzyldithiocarbamato)indium(III) (1) with hydrogens. Atoms are represented by ellipsoids at 50% probability.
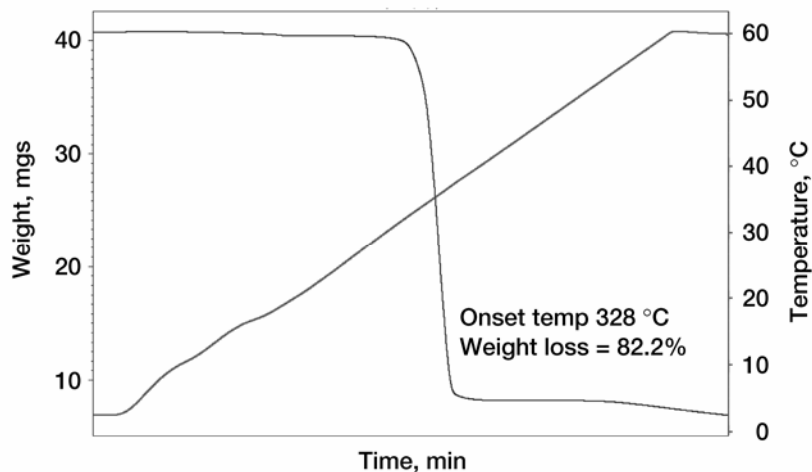

Onset temp 328 °C
Weight loss = 82.2%

Figure 2.—Typical thermogravimetric analysis plot the decomposition of (1).
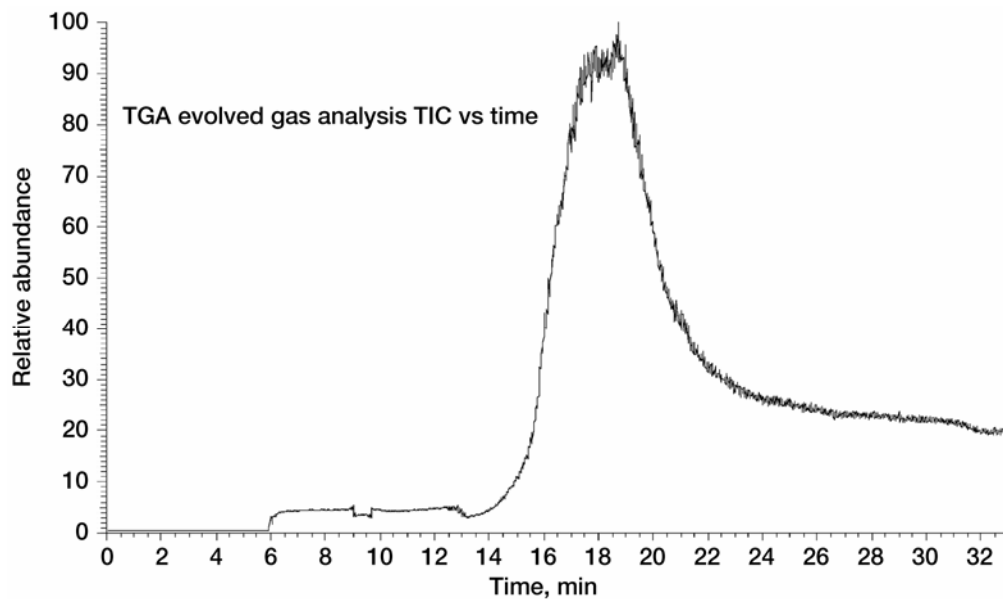
Figure 3.—Mass spectral analysis of the exhaust gases from the decomposition of (1).
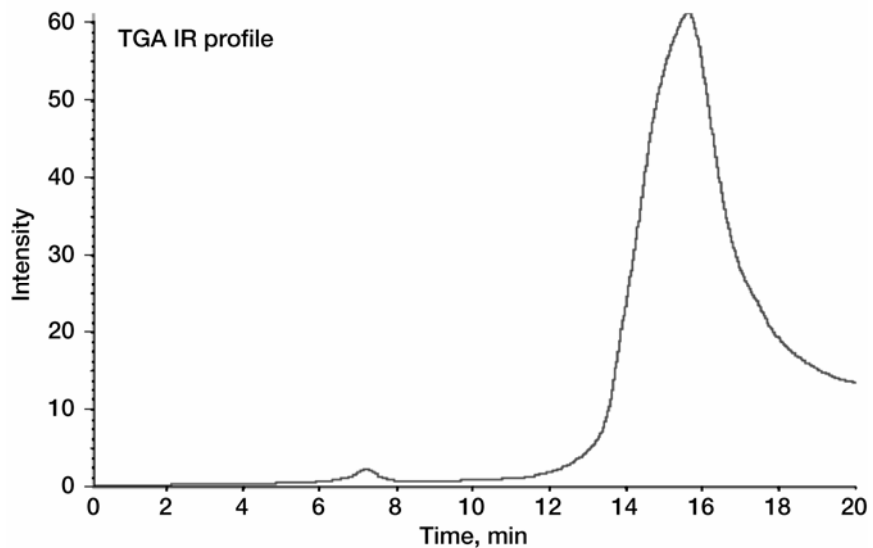

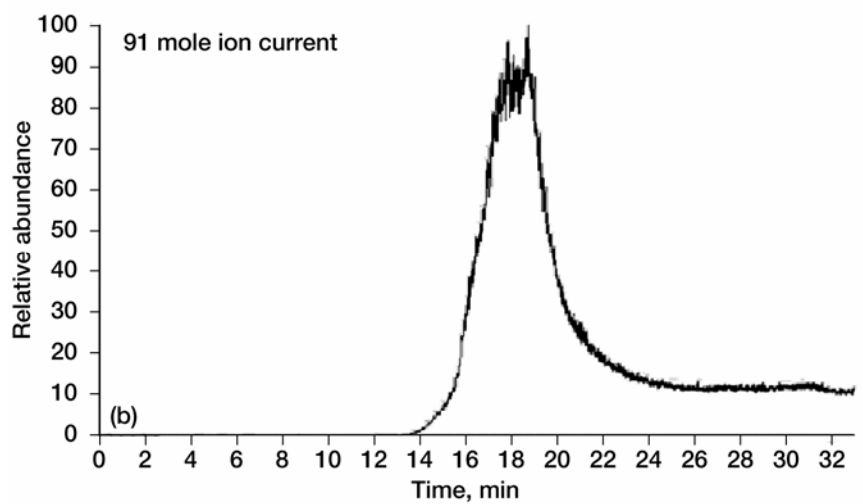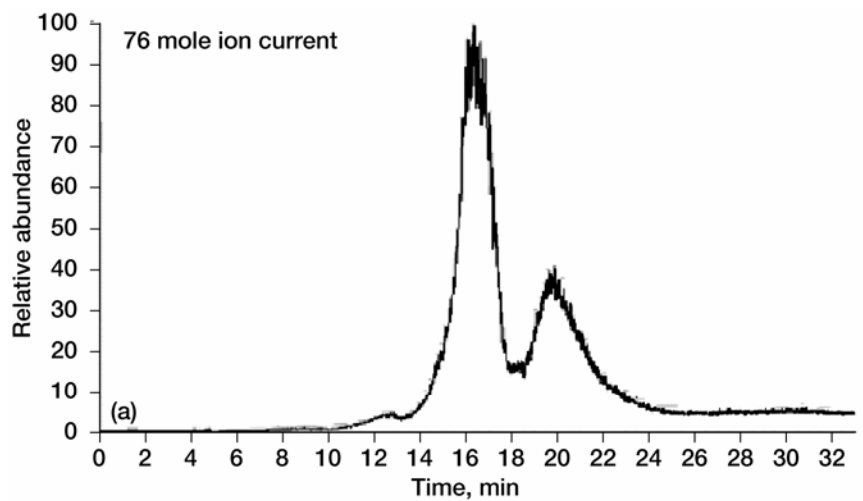Figure 4.—FTIR profile of the exhaust gases from the decomposition of (1).

Figure 5.—Profile of the m/e = 76 (a) and m/e = 91 (b) ion peaks as a function of time from the mass spectral analysis of the exhaust gases from decomposition of tris(N,N-dibenzyldithiocarbamato)indium(III) (1).
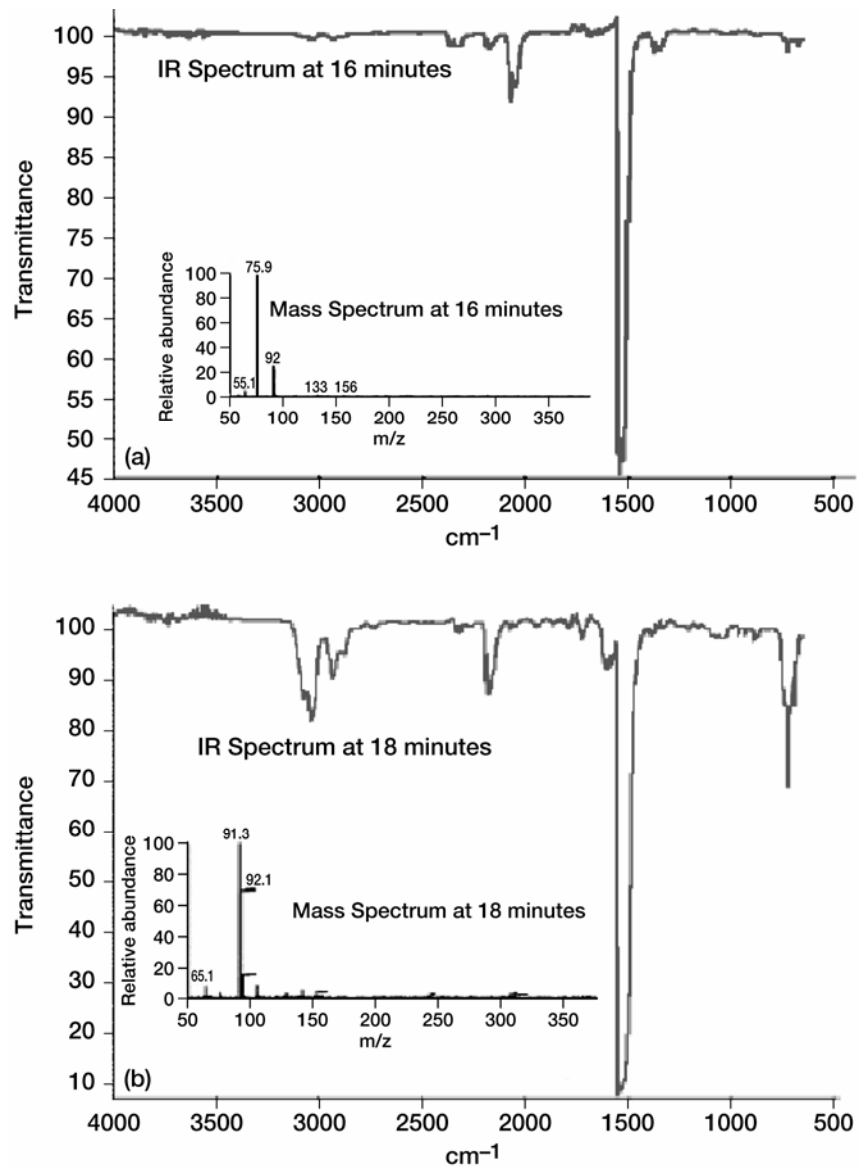
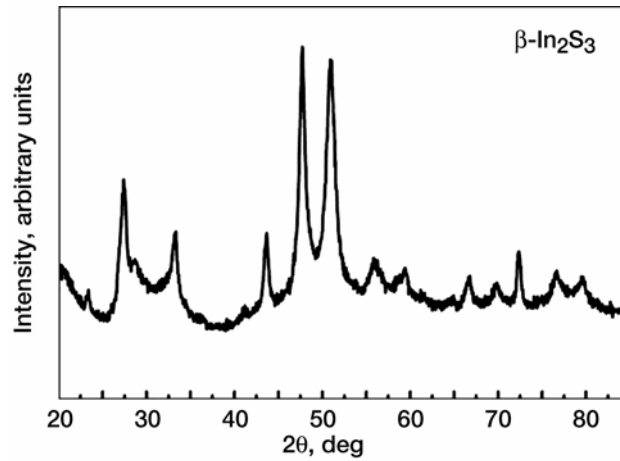Figure 6.—FTIR and mass spectrum (inset) of the exhaust gases from decomposition of (1) at 16 (a) and 18 (b) minute mark.

Figure 7.—XRD powder pattern of the solid product which resulted from the thermal decomposition of tris(N,N-dibenzyldithiocarbamato)indium(III) (1).
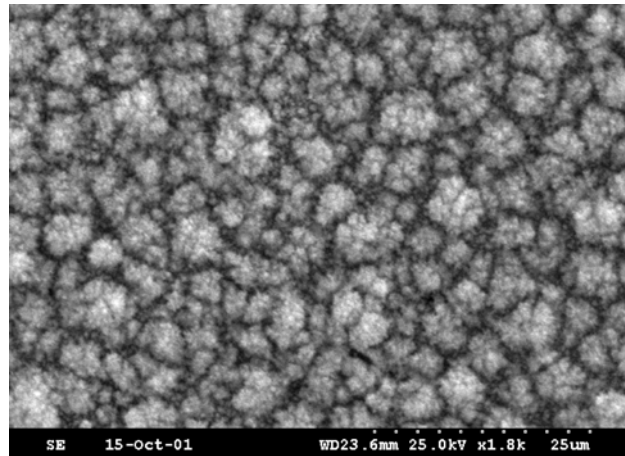

Figure 8.—SEM image of CuInS$_2$ film deposited from (1) at 425 °C from a 0.005 M solution using 2 slpm of argon carrier gas onto Cu on Ti substrate. EDS analysis shows a near stoichiometric film. Magnification is 1.8 K and the barscale is 25 μm.
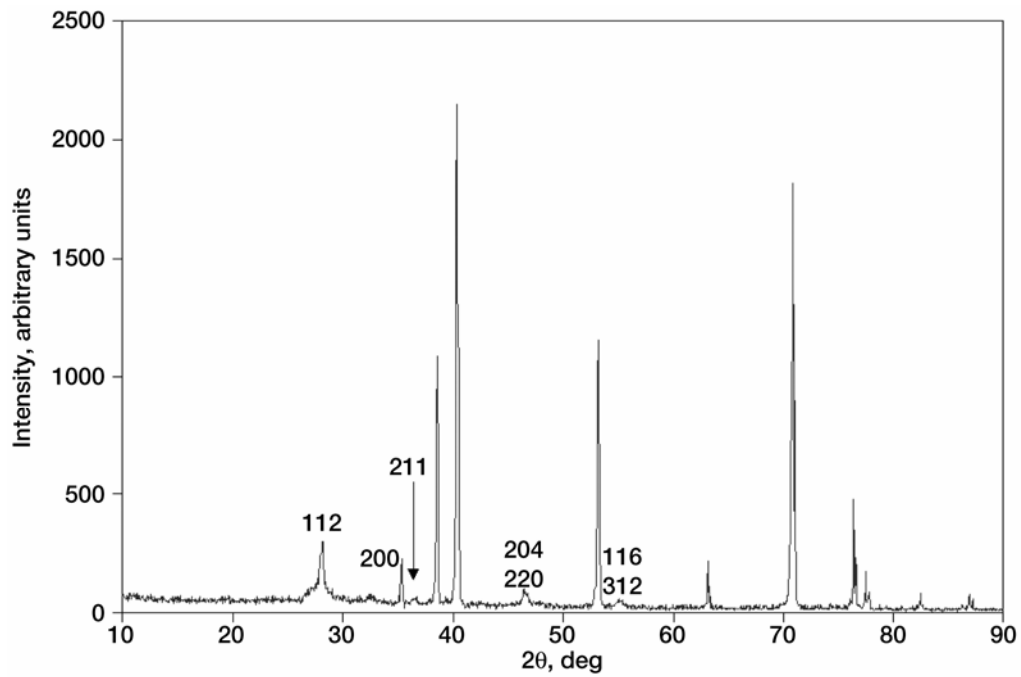
Figure 9.—XRD pattern of a CuInS$_2$ film deposited from (1) at 425 °C from a 0.005 M solution using 2 slpm of argon carrier gas. Unlabeled peaks are attributed to the titanium substrate.

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13. ABSTRACT (Maximum 200 words)

Tris(bis(phenylmethyl)carbamodithioato-S,S'), commonly referred to as tris(N,N-dibenzyldithiocarbamato)indium(III), $In(S_2CNBz_2)_3$, was synthesized and characterized by single crystal X-ray crystallography. The compound crystallizes in the triclinic space group P1 bar with two molecules per unit cell. The material was further characterized using a novel analytical system employing the combined powers of thermogravimetric analysis, gas chromatography/mass spectrometry and Fourier-Transform infrared spectroscopy to investigate its potential use as a precursor for the chemical vapor deposition (CVD) of thin film materials for photo-voltaic applications. Upon heating, the material thermally decomposes to release CS_2 and benzyl moieties in to the gas phase, resulting in bulk In_2S_3. Preliminary spray CVD experiments indicate that $In(S_2CNBz_2)_3$ decomposed on a Cu substrate reacts to produce stoichiometric $CuInS_2$ films.

14. SUBJECT TERMS

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