Novel Bimetallic Thiocarboxylate Compounds as Single-Source Precursors to Binary and Ternary Metal Sulfide Materials

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The binuclear compounds $[(Ph_3P)CuM(SC\{O\}Ph)_4]$ (M = Ga (**1**) or In (**2**)), $[(Ph_3P)_2AgGa(SC\{O\}Ph)_4]$ (**3**), $[(Ph_3P)_2AgIn(SC\{O\}R)_4]$ (R = Me (**4**) or Ph (**5**)) have been synthesized and characterized. The solid-state structures of compounds **1**−**3** have been determined by X-ray crystallography. Thermogravimetry and pyrolysis studies revealed that these compounds decompose to give the corresponding ternary metal sulfide materials. However, using the aerosol-assisted chemical vapor deposition (AACVD) method, In_2S_3 thin films were obtained from **2** and $AgIn_5S_8$ thin films were obtained from compounds **4** and **5**.

Introduction

Metal sulfides find a wide variety of applications, e.g., in photovoltaics and optoelectronic devices, and hence there has been considerable interest in synthesizing single-source precursors for these materials.[1−4] Such precursors have been considered as attractive sources for bulk materials, thin films, or nanoparticles. Among such materials, $CuInS_2$ with a band gap of 1.53 eV at ambient temperature is considered a good candidate for photovoltaic applications.[5] Solar cells fabricated with thin films of $CuInS_2$ have light-conversion efficiencies of ca. 7%.[6] $CuGaS_2$ has a wide band gap (2.49 eV) and is used in green light emitting diodes.[7] $AgInS_2$, $AgIn_5S_8$, and $AgGaS_2$ are used as linear and nonlinear optical materials.[8,9] Despite these many potential applications for ternary materials such as $MM'S_2$ (M = Cu or Ag and M′ = Ga or In), single-source precursors for these materials are rare. Kanatzidis et al. have prepared and characterized compounds of the general formula $(Ph_3P)_2Cu(\mu\text{-}ER)_2In(ER)_2$ (E = S or Se and R = Et or *iso*-Bu). The single-crystal structures of these compounds have also been reported.[10] These compounds, when subjected to pyrolysis, yielded the corresponding ternary materials. Buhro and co-workers have used $(Ph_3P)_2Cu(\mu\text{-}SEt)_2In(SEt)_2$ to obtain thin films of $CuInS_2$ using spray MOCVD.[11] Nomura et al. have prepared a compound of the formula $[Bu_2In(SPr)Cu(S_2CNPr_2)]$ and used it to deposit thin films of $CuInS_2$.[12] These authors have also reported the deposition of $CuInS_2$ by solution pyrolysis of Bu_2InSPr and $Cu(S_2CNBu_2)_2$.[13] Recently, two liquid compounds, $[(n\text{-}Bu_3P)_2Cu(SR)_2In(SR)_2]$ (R = Et and *n*-Pr) have been successfully used to deposit $CuInS_2$ thin films.[14,15] As a part of our ongoing explorations of metal−thiocarboxylate systems,[16−27] we have now devoted attention to the syntheses of single-source molec-

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ular precursors for I−III−VI materials. A preliminary account of this study has been published earlier.[28] In this paper we report on the synthesis and characterization of compounds of the type $[(Ph_3P)CuM(SC\{O\}Ph)_4]$ (M = Ga (**1**) or In (**2**)), $[(Ph_3P)_2AgGa(SC\{O\}Ph)_4]$ (**3**), and $[(Ph_3P)_2AgIn(SC\{O\}R)_4]$ (R = Me (**4**) or Ph(**5**)), their thermal properties, and results of AACVD experiments.

Experimental Section

General. All materials were obtained commercially and used as received. The solvents were dried by allowing them to stand over 3-Å molecular sieves overnight. The preparations were carried out under nitrogen atmosphere and the yields are reported with respect to the metal salts. The compounds are fairly stable but were stored under nitrogen at 5 °C to avoid any decomposition. The starting material $Ga(NO_3)_3{\cdot}xH_2O$ ($x \approx 3$ by TG analysis) was purchased from Aldrich and $[(Ph_3P)_2Cu(NO_3)]$ was prepared by a literature method.[29] Compounds **4** and **5** were prepared as described earlier.[28]

Synthesis of $[(PPh_3)Cu(\mu\text{-}SC\{O\}Ph\text{-}S,O)(\mu\text{-}SC\{O\}Ph\text{-}S,O)_2Ga(SC\{O\}Ph)]$ (1). To NaSC{O}Ph formed in situ (by reacting PhC{O}SH (184 μL, 1.56 mmol) and Na (0.04 g, 1.56 mmol) in MeOH (15 mL)), 0.1 g of $Ga(NO_3)_3{\cdot}3H_2O$ (0.32 mmol) in MeOH (10 mL) was added to get a yellow solution and was followed by the addition of $(Ph_3P)_2Cu(NO_3)$ (0.25 g, 0.39 mmol) in CH_2Cl_2 (15 mL). The orange solution thus obtained was stirred and the solvents were removed under a flow of N_2. The product obtained as red oil along with some yellow powder was extracted with CH_2Cl_2 (20 mL), and the resulting red solution was separated and layered with petroleum ether. Reddish yellow crystals were obtained the following day. The crystals of **1** were collected, washed with petroleum ether, and dried under vacuum. Yield 0.27 g (89%); mp 163 °C (decomposition). Anal. Calcd for $C_{46}H_{35}O_4S_4PCuGa$ (mol wt 944.29): C, 58.51; H, 3.74. Found: C, 58.48; H, 3.77. ^{13}C NMR ($CDCl_3$) δ, ppm thiobenzoato ligand: 127.3 ($C_{2/6}$ or $C_{3/5}$), 128.3 ($C_{2/6}$ or $C_{3/5}$), 131.4 (C_4), 138.8 (C_1), 202.9 (Ph*C*OS). PPh_3: 128.6 (C_3, ^3J(P−C) = 8.7 Hz), 129.6 (C_4), 132.9 (C_1, ^1J(P−C) = 27.2 Hz), 133.7 (C_2, ^2J(P−C) = 15.2 Hz). ^{31}P NMR: δ, ppm −1.54 (s). Selected IR data: 1594.9 (w, C═O) and 983.7 (s, C−S) cm^{-1}.

Synthesis of $[(PPh_3)Cu(\mu\text{-}SC\{O\}Ph\text{-}S,O)_2(\mu_2\text{-}SC\{O\}Ph\text{-}S_2,O)In(SC\{O\}Ph)]$ (2). The compound was synthesized using a procedure similar to **1** but $Ga(NO_3)_3{\cdot}3H_2O$ was replaced by $InCl_3{\cdot}4H_2O$. Yield 69%; mp 185 °C (melting with decomposition). Anal. Calcd for $C_{46}H_{35}O_4S_4PCuIn{\cdot}0.5\ CH_2Cl_2$ (mol wt 1031.85): C, 54.13; H, 3.52. Found: C, 54.38; H, 3.74. ^{13}C NMR ($CDCl_3$) δ, ppm thiobenzoato ligand: 127.9 ($C_{2/6}$ or $C_{3/5}$), 129.3 ($C_{2/6}$ or $C_{3/5}$), 133.1 (C_4), 137.7 (C_1), 206.7 (Ph*C*OS). PPh_3: 128.5 (C_3, ^3J(P−C) = 8.7 Hz), 129.6 (C_4), 132.8 (C_1, ^1J(P−C) = 20.0 Hz), 133.7 (C_2, ^2J(P−C) = 14.2 Hz). ^{31}P NMR: δ, ppm −1.57. Selected IR data: 1594.5 (s, C═O), 950.0 (s, C−S) cm^{-1}.

$[(PPh_3)_2Ag(\mu\text{-}SC\{O\}Ph\text{-}S)Ga(SC\{O\}Ph)_3]$ (3). A solution of PPh_3 (0.21 g, 0.78 mmol) in 15 mL of MeCN was added to a solution of $AgNO_3$ (0.07 g, 0.39 mmol) in 10 mL of MeCN and stirred for about 10 min to obtain a precipitate of $(PPh_3)_2AgNO_3$. The solvents were evaporated, and the resulting white solid, dissolved in 20 mL of $CHCl_3$, was added to $Ga(NO_3)_3{\cdot}3H_2O$ (0.1 g, 0.39 mmol) in 12 mL of MeOH. To this solution, C_6H_5COSNa (prepared in situ by reacting C_6H_5COSH (184 μL, 1.56 mmol) with Na (0.036 g, 1.564 mmol) in 15 mL of MeOH) was added. The resulting bright yellow solution was stirred for 30 min and then the solvents were removed by a flow of N_2. The product was extracted with $CHCl_3$ (15 mL) and filtered immediately, and the filtered product was layered with petroleum ether and stored at 5 °C. Colorless crystals of **3** thus obtained were filtered, washed with Et_2O, and dried under vacuum. Yield 0.37 g (76%); mp 167 °C (melting with decomposition). Anal. Calcd for $C_{64}H_{50}O_4S_4P_2AgGa$ (mol wt 1250.9): C, 61.45; H, 4.02. Found: C, 61.87; H, 4.06. ^{13}C NMR ($CDCl_3$) δ, ppm thiobenzoic acid ligand: 127.7 ($C_{2/6}$ or $C_{3/5}$), 128.3 ($C_{2/6}$ or $C_{3/5}$), 131.6 (C_4), 140.6 (C_1), 201.0 (Ph*C*OS). PPh_3: 128.6 (C_3, ^3J(P−C) = 9.8 Hz), 129.7 (C_4), 133.0 (C_1, ^1J(P−C) = 20.7 Hz), 133.8 (C_2, ^2J(P−C) = 16.3 Hz). ^{31}P NMR: δ, ppm 6.53. IR data (cm^{-1}): 1569.4 (s, C═O), 973.8 (w, C−S).

Instruments and Characterization. The $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker ACF300 FTNMR spectrometer using TMS as internal and 85% H_3PO_4 as external reference at 25 °C. The IR spectra (KBr pellet) were recorded using a Bio-Rad FTIR spectrometer. The elemental analyses were performed by the microanalytical laboratory of the chemistry department, National University of Singapore. Thermogravimetric analyses were carried out using a SDT 2980 TGA thermal analyzer with a heating rate of 10 °C min^{-1} in N_2 atmosphere using a sample size of 5−10 mg per run. X-ray powder patterns were obtained using a D5005 Bruker AXS X-ray diffractometer. Pyrolysis experiments were carried out in a horizontal tube furnace in a quartz reaction chamber. The quartz reactor was subjected to dynamic vacuum of about 0.5 Torr. The SEM images were obtained from a JEOL JSM-T220A instrument for bulk materials and a Philips XL30 FEG for thin films and EDAX analyses. The XPS measurements were performed in the ultrahigh vacuum chamber (base pressure of 10^{-8} Pa) of an ESCA 300 spectrometer using Mg Kα excitation. The energy scale was calibrated using Au and argon ions were used for etching.

X-ray Crystallography. The diffraction experiments were carried out at 20 °C on a Bruker SMART CCD diffractometer with Mo Kα radiation from a sealed tube. The program SMART[30] was used for collecting frames of data, indexing reflections, and determination of lattice parameters; SAINT[30] was used for integration of the intensity of reflections and scaling. SADABS[31] was used for absorption correction, and SHELXTL[32] was used for space group and structure determination and least-squares refinements on F^2. The relevant crystallographic data and refinement details are shown in Table 1. The phenyl ring of the thiobenzoate anion (C31−C36) in **1** was found to be disordered. Two disorder models with equal occupancies were refined for the same. There are 3.5 $CHCl_3$ solvent molecules present in **3**. All the solvent molecules were disordered and were treated with a soft SADI restraint on C−Cl and Cl··Cl distances. Disorder models were resolved for the $CHCl_3$ molecules. One molecule is disordered over two positions with occupancies of 0.55 and 0.45. Another $CHCl_3$ molecule is disordered over three locations with occupancies of 0.6, 0.25, and 0.15. The half molecule of $CHCl_3$ present in **3** is also disordered over two locations with occupancies of 0.3 and 0.2.

Aerosol-Assisted Chemical Vapor Deposition (AACVD). Approximately 0.25 g of precursor was dissolved in 30 mL of toluene (or THF) in a round-bottomed flask. Six glass substrates (1 × 2 cm) were placed inside the reactor tube. The carrier gas flow rate was controlled by Platon flow gauges. The solution in the flask was placed in a water bath above the piezoelectric modulator of a humidifier in which aerosol droplets were generated and transferred by the carrier gas (N_2, flow rate 180 sccm) into the hot-wall zone. Then both the solvent and the precursor were evaporated, and the precursor vapor reached the heated substrate surface where thermally induced reactions and film deposition took place. This homemade aerosol-assisted chemical vapor deposition kit consisted of a two-necked flask, a PIFCO ultrasonic humidifier (model 1077) and a Carbolite furnace.

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Table 1. Crystal Data and Structure Refinement for 1−3

	1	2	3
chemical formula	$C_{46}H_{35}CuGaO_4PS_4$	$C_{46}H_{35}CuInO_4PS_4 \cdot 0.5\ CH_2Cl_2$	$C_{64}H_{50}O_4S_4P_2AgGa \cdot 3.5\ CHCl_3$
formula weight	944.21	1031.77	1668.60
temperature, °C	20	20	−50
λ, Å	0.71073	0.71073 Å	0.71073
crystal system	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
unit cell dimensions			
a, Å	13.0239(2)	10.5914(1)	15.0668(7)
b, Å	9.2656(2)	11.8903(1)	15.3124(7)
c, Å	36.1156(8)	19.6156(3)	18.6217(8)
α, deg	90	74.151(1)	101.240(1)
β, deg	94.320(1)	77.889(1)	113.171(1)
γ, deg	90	77.254(1)	95.551(1)
V, Å^3	4345.8(2)	2288.19(5)	3801.6(3)
Z	4	2	2
ρ, g/cm^3	1.443	1.498	1.458
μ, mm^{-1}	1.381	1.286	1.177
F(000)	1928	1042	1682
θ range, deg	1.86 to 26.37	1.81 to 26.37	2.04 to 25.00
index ranges	$-16 \le h \le 16$	$-13 \le h \le 12$	$-17 \le h \le 17$
	$-11 \le k \le 11$	$-14 \le k \le 13$	$-18 \le k \le 15$
	$-30 \le l \le 45$	$-24 \le l \le 16$	$-17 \le l \le 22$
reflections collected	22503	13171	22382
independent reflections	8684, $R_{int} = 0.0670$	8996, $R_{int} = 0.0272$	13374, $R_{int} = 0.0219$
data/restraints/parameters	8684/0/474	8996/1/542	13374/84/803
GOF on F^2	1.094	1.054	1.028
final R indices ($I > 2\sigma(I)$)	R1 = 0.0858	R1 = 0.0398	R1 = 0.0670
	wR2 = 0.1903	wR2 = 0.1105	wR2 = 0.1989
R indices (all data)	R1 = 0.1327	R1 = 0.0531	R1 = 0.0852
	wR2 = 0.2161	wR2 = 0.1162	wR2 = 0.2124
extinction coefficient		0.0010(3)	
largest difference peak and hole, e·Å^{-3}	1.180 and −0.783	1.081 and −0.656	2.003 and −1.320

Results and Discussion

Synthesis. The compounds $[(Ph_3P)Cu(\mu\text{-}SC\{O\}Ph)_3M(SC\{O\}Ph)]$ (M = Ga(**1**) or In(**2**)) were prepared by reacting bis-triphenylphosphinecopper(I) nitrate with the appropriate $[M(SC\{O\}Ph)_4]^-$ anion as shown below in eq 1. In the resulting bimetallic complexes the copper atoms are bonded to the sulfur centers of the thiobenzoate ligands and only to one PPh_3 unit.

$$(Ph_3P)_2Cu(NO_3) + MX_3 + 4NaSC\{O\}Ph \rightarrow NaNO_3 + 3NaX + PPh_3 + [(Ph_3P)Cu(SC\{O\}Ph)_3M(SC\{O\}Ph)] \quad (M = Ga\ (\mathbf{1});\ In\ (\mathbf{2})) \quad (1)$$

Attempts to isolate the thioacetate analogues of **1** and **2** using a similar synthetic method were unsuccessful. Compounds **1** and **2** were fairly stable, however, they were stored at 5 °C in sample vials purged with nitrogen. From reactions of $(Ph_3P)_2Ag(NO_3)$ with the $[M(SC\{O\}R)_4]^-$ anion, no pure bimetallic compounds could be isolated. Hence, the synthetic route was slightly modified as follows. The bis-triphenylphosphine silver salts were premixed with the corresponding indium or gallium salts followed by the addition of the sodium thiocarboxylate. The reactions are summarized below (eq 2 or 3). These reactions yielded pure **3**−**5**.

$$(Ph_3P)_2Ag(NO_3) + Ga(NO_3)_3 \cdot 3H_2O + 4NaSC\{O\}Ph \rightarrow [(Ph_3P)_2Ag(\mu\text{-}SC\{O\}Ph)Ga(SC\{O\}Ph)_3] + 4NaNO_3 \quad (2)$$

$$(Ph_3P)_2AgCl + InCl_3 \cdot 4H_2O + 4NaSC\{O\}R \rightarrow [(Ph_3P)_2Ag(\mu\text{-}SC\{O\}Ph)In(SC\{O\}R)_3] + 4NaCl \quad (R = Me\ (\mathbf{4});\ Ph\ (\mathbf{5})) \quad (3)$$

However, under similar conditions we were unable to isolate $[(Ph_3P)_2AgGa(SC\{O\}Me)_4]$. Attempts to synthesize **4** and **5** at room temperature led to decomposition of the compounds, hence they were synthesized at 0 °C.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of 1

Bond Lengths			
Cu(1)−S(1)	2.488(2)	Cu(1)−S(2)	2.265(2)
Cu(1)−S(3)	2.266(2)	Cu(1)−P(1)	2.266(2)
Ga(1)−S(1)	2.268(2)	Ga(1)−S(4)	2.240(2)
Ga(1)−O(2)	1.870(5)	Ga(1)−O(3)	1.879(5)
S(1)−C(1)	1.788(8)	S(2)−C(2)	1.666(7)
S(3)−C(3)	1.671(8)	S(4)−C(4)	1.767(8)
O(1)−C(1)	1.222(9)	O(2)−C(2)	1.280(8)
O(3)−C(3)	1.256(8)	O(4)−C(4)	1.229(9)
Bond Angles			
S(2)−Cu(1)−S(1)	107.66(8)	S(3)−Cu(1)−S(1)	102.26(7)
S(2)−Cu(1)−S(3)	119.17(9)	P(1)−Cu(1)−S(1)	113.17(7)
S(2)−Cu(1)−P(1)	105.94(8)	S(3)−Cu(1)−P(1)	108.86(7)
S(4)−Ga(1)−S(1)	117.69(8)	O(2)−Ga(1)−S(1)	121.2(2)
O(3)−Ga(1)−S(1)	113.8(2)	O(2)−Ga(1)−S(4)	99.1(2)
O(3)−Ga(1)−S(4)	102.2(2)	O(2)−Ga(1)−O(3)	99.7(3)
Ga(1)−S(1)−Cu(1)	79.39(6)	C(1)−S(1)−Cu(1)	110.6(3)
C(2)−S(2)−Cu(1)	111.5(3)	C(3)−S(3)−Cu(1)	113.3(2)
C(1)−S(1)−Ga(1)	90.5(3)	C(4)−S(4)−Ga(1)	96.9(3)
C(2)−O(2)−Ga(1)	132.6(5)	C(3)−O(3)−Ga(1)	133.6(5)
O(1)−C(1)−S(1)	118.7(6)	O(2)−C(2)−S(2)	125.8(6)
O(3)−C(3)−S(3)	124.9(5)	O(4)−C(4)−S(4)	120.8(7)

Structure of $[(PPh_3)Cu(\mu\text{-}SC\{O\}Ph\text{-}S)(\mu\text{-}SC\{O\}Ph\text{-}S,O)_2Ga(SC\{O\}Ph)]$ (1). A perspective view of **1** is shown in Figure 1 and selected bond lengths and angles are given in Table 2. In **1**, both the metal atoms, Cu(1) and Ga(1), are present in distorted tetrahedral geometry. The copper atom is bonded to one triphenylphosphine ligand and three sulfur atoms of three thiobenzoato ligands. All three thiobenzoato ligands bridge the two metal centers: two $PhC\{O\}S^-$ anions through a μ_2-*S*,*O*, and the other in a μ_2-*S* fashion. The distorted tetrahedral coordination environment at Ga(1) is made up by a S_2O_2 donor set. The P(1)−Cu(1)

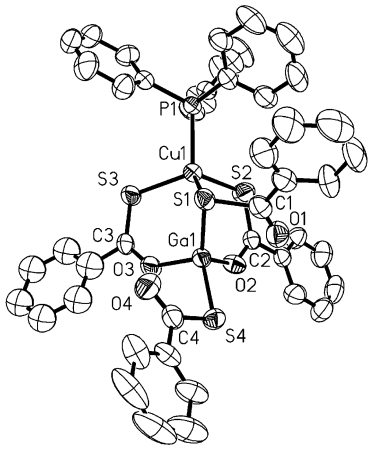

Figure 1. ORTEP diagram (with 50% probability of displacement ellipsoids) showing the molecular structure of **1**. Hydrogen atoms have been omitted for clarity.

distance, (2.266(2) Å) observed in **1** is normal.[22] The Cu(1)−S(1) distance, 2.488(2) Å, is longer than Cu(1)−S(2) and Cu(1)−S(3) (2.265(2) and 2.266(2) Å, respectively) because S(1) is also involved in bonding to the Ga atom. The Cu−S distances from bridging sulfur atoms are expected to be longer than those from nonbridging ligands.[21,22,24] Further, the shortening of C−S and lengthening of C−O distances may be attributed to the delocalization of electrons at the thiocarboxylate groups containing C(2) and C(3) atoms. A similar trend was observed in the other triphenylphosphinecopper thiocarboxylate compounds.[22] The Ga(1)−S(1) and Ga(1)−S(4) distances, 2.268(2) and 2.240(2) Å, respectively, are not equal as expected for the bridging and terminal Ga−S bonds. The Ga(1)−O(2) and Ga(1)−O(3) distances, 1.870(5) and 1.879(5) Å respectively, fall within the range of established Ga−O distances (1.780−2.020 Å) obtained from the Cambridge Structure Database.[33] The Ga(1)−O(1) and Ga(1)−O(4) distances, 2.690(6) and 2.913(7) Å, respectively, are significantly less than the sum of van der Waals radii, 3.4 Å, and represent very weak interactions. Further, the distorted tetrahedral geometry at Ga(1) (99.1−121.2°) appears to support this.

Structure of [(PPh$_3$)Cu(μ-SC{O}Ph-*S,O*)$_2$(μ_2-SC{O}Ph-*S$_2$,O*)In(SC{O}Ph)] (2). A view of **2** is shown in Figure 2 and selected bond lengths and angles are given in Table 3. Compound **2** is a bimetallic compound containing copper and indium atoms. Of these, Cu(1) is bonded to one triphenylphosphine ligand and three thiobenzoate anions through their sulfur donor sites forming a tetrahedral $PCuS_3$ core as in **1**. Three thiobenzoate anions bridge the two metal ions through two μ_2-*S,O* and one μ_2-*S*$_2$,*O* bonding modes. The fourth thiobenzoate anion chelates the indium metal atom. The coordination environment about the In(1) atom is thus distorted octahedral with a InO_4S_2 core. The P(1)−Cu(1) distance, 2.283(1) Å, is slightly longer than the corresponding bond distance observed in **1**. The Cu(1)−S(1) and Cu(1)−S(2) distances (2.265(1) and 2.281(1) Å, respectively) are longer than the Cu(1)−S(3) distance (2.470(1) Å) because of different types of bonding modes as explained above for **1**. It was also observed that the

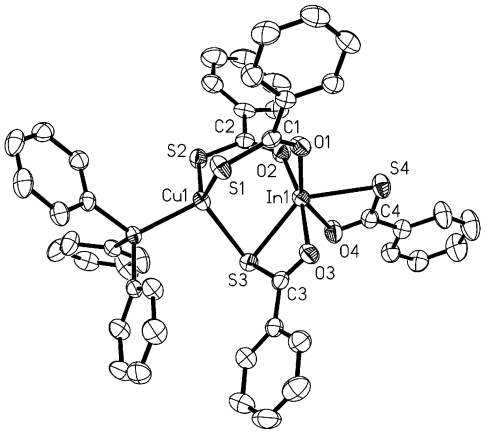

Figure 2. Thermal ellipsoid plot showing a view of **2**. Hydrogen atoms are not shown.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of 2

Bond Lengths			
Cu(1)−S(1)	2.265(1)	Cu(1)−S(2)	2.281(1)
Cu(1)−S(3)	2.470(1)	Cu(1)−P(1)	2.283(1)
In(1)−S(3)	2.537(1)	In(1)−S(4)	2.503(1)
In(1)−O(1)	2.126(3)	In(1)−O(2)	2.139(3)
In(1)−O(3)	2.372(3)	In(1)−O(4)	2.386(3)
In(1)−Cu(1)	3.068(1)	S(1)−C(1)	1.679(4)
S(2)−C(2)	1.680(4)	S(3)−C(3)	1.762(4)
S(4)−C(4)	1.726(4)	O(1)−C(1)	1.275(4)
O(2)−C(2)	1.273(4)	O(3)−C(3)	1.239(4)
O(4)−C(4)	1.240(4)	In(1)··Cu(1)	3.068(1)
Bond Angles			
S(1)−Cu(1)−S(2)	118.58(4)	S(1)−Cu(1)−S(3)	114.95(4)
S(2)−Cu(1)−S(3)	104.06(4)	S(1)−Cu(1)−P(1)	109.95(4)
S(2)−Cu(1)−P(1)	106.26(4)	P(1)−Cu(1)−S(3)	101.34(4)
S(4)−In(1)−S(3)	136.62(4)	O(1)−In(1)−S(3	124.76(7)
O(2)−In(1)−S(3)	108.43(7)	O(3)−In(1)−S(3)	63.38(7)
O(4)−In(1)−S(3)	83.97(7)	O(1)−In(1)−S(4)	89.37(7)
O(2)−In(1)−S(4)	96.19(7)	O(3)−In(1)−S(4)	94.86(7)
O(4)−In(1)−S(4)	63.30(7)	O(1)−In(1)−O(2)	89.8(1)
O(1)−In(1)−O(3)	89.4(1)	O(2)−In(1)−O(3)	168.92(9)
O(1)−In(1)−O(4)	150.9(1)	O(2)−In(1)−O(4)	83.9(1)
O(3)−In(1)−O(4)	101.9(1)	C(1)−S(1)−Cu(1)	112.2(1)
C(2)−S(2)−Cu(1)	114.9(1)	C(3)−S(3)−Cu(1)	105.7(1)
Cu(1)−S(3)−In(1)	75.55(3)	C(3)−S(3)−In(1)	80.2(1)
C(4)−S(4)−In(1)	81.1(1)	C(1)−O(1)−In(1)	129.5(2)
C(2)−O(2)−In(1)	130.2(2)	C(3)−O(3)−In(1)	98.4(2)
C(4)−O(4)−In(1)	96.6(2)	O(1)−C(1)−S(1)	124.6(3)
O(2)−C(2)−S(2)	125.5(3)	O(3)−C(3)−S(3)	117.7(3)
O(4)−C(4)−S(4)	119.0(3)		

In(1)−O(1) and In(1)−O(2) distances (2.126(3) and 2.139(3) Å, respectively) are shorter than the In(1)−O(3) and In(1)−O(4) distances (2.372(3) and 2.386(3) Å, respectively). The former In−O distances fall in the upper range of distances observed in a few indium alkoxide compounds, 1.969−2.152 Å.[34] The shorter In−O distance may be attributed to extra negative charges acquired by O(1) and O(2) due to the delocalization of electrons in these thiocarboxylate groups. The lengthening of C−O and shortening of C−S bonds appear to suggest this. On the other hand, the longer In−O distances may be attributed to the weakening of the bond between In(III) and neutral carbonyl oxygen atom as indicated by the C═O distances in Table 3. The thiobenzoato ligands adopt three types of bonding modes: a terminal chelating mode, a bridging mode with the O atoms linked to indium and the S atoms to copper, and a terminal chelating mode with an additional Cu−S bond. The nonbonding distance Cu(1)···

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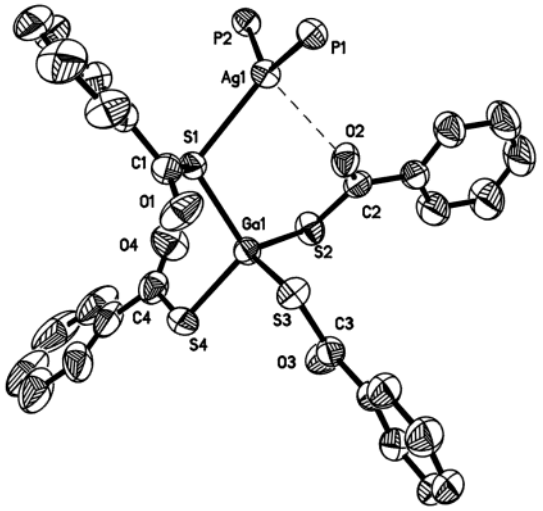

Figure 3. Perspective view of **3**.

Table 4. Selected Bond Lengths (Å) and Angles (deg) of 3

Bond Lengths			
Ag(1)−S(1)	2.623(2)	Ag(1)−P(1)	2.451(2)
Ag(1)−P(2)	2.455(2)	Ga(1)−S(1)	2.309(2)
Ga(1)−S(2)	2.271(2)	Ga(1)−S(3)	2.273(2)
Ga(1)−S(4)	2.271(2)	S(1)−C(1)	1.778(6)
S(2)−C(2)	1.761(6)	S(3)−C(3)	1.766(6)
S(4)−C(4)	1.761(7)	O(1)−C(1)	1.193(7)
O(2)−C(2)	1.216(7)	O(3)−C(3)	1.198(7)
O(4)−C(4)	1.215(8)		
Bond Angles			
P(1)−Ag(1)−S(1)	120.86(5)	P(2)−Ag(1)−S(1)	105.66(5)
P(1)−Ag(1)−P(2)	129.14(5)	S(2)−Ga(1)−S(1)	106.21(6)
S(3)−Ga(1)−S(1)	115.00(6)	S(4)−Ga(1)−S(1)	107.10(6)
S(2)−Ga(1)−S(3)	112.99(6)	S(2)−Ga(1)−S(4)	113.00(7)
S(4)−Ga(1)−S(3)	102.55(7)	Ga(1)−S(1)−Ag(1)	109.26(6)
C(1)−S(1)−Ag(1)	99.5(2)	C(1)−S(1)−Ga(1)	104.4(2)
C(2)−S(2)−Ga(1)	97.5(2)	C(3)−S(3)−Ga(1)	97.4(2)
C(4)−S(4)−Ga(1)	101.1(3)	O(1)−C(1)−S(1)	121.6(5)
O(2)−C(2)−S(2)	122.9(5)	O(3)−C(3)−S(3)	123.2(5)
O(4)−C(4)−S(4)	121.9(5)		

In(1), 3.068(1) Å, is shorter than the sum of their van der Waals radii (3.3 Å)[35] as was also observed in $(Ph_3P)_2$-$Cu(\mu$-$SEt)_2In(SEt)_2$, $(Ph_3P)_2Cu(\mu$-$SeEt)_2In(SeEt)_2$, and $(Ph_3P)_2Cu(\mu$-$S(iso$-$Bu))_2In(S(iso$-$Bu)_2$, which are 3.34, 3.32, and 3.24 Å, respectively.[10] The origin of this bond shortening has not been investigated further. However, the longer Cu−P distance, 2.283(1) Å, as compared to **1** may be a consequence of this Cu··In weak interaction. The In(1) has a highly distorted octahedral environment with S_2O_4 donor set. The In−S distances, 2.537(1) and 2.503(1) Å, are comparable to 2.457(1)−2.542(1) Å observed in **5** which also has highly distorted octahedral geometry at In(III).[28]

Structure of $[(Ph_3P)_2Ag(\mu$-SC{O}Ph-*S*$)Ga(SC\{O\}Ph)_3]$ (3). A perspective view of **3** is shown in Figure 3 and selected bond lengths and angles are listed in Table 4. Compound **3** crystallizes with 3.5 $CHCl_3$ molecules. It consists of one anionic $[Ga(SC\{O\}Ph)_4]$ and a cationic $[(Ph_3P)_2Ag]$ unit. All four thiobenzoate anions are S-bonded to the gallium ion, Ga(1), and hence it has a tetrahedral GaS_4 core. One thiobenzoate anion adopts a sulfur atom, S(1) in its bridging mode to bind Ga(1) and Ag(1). The distance between Ag(1) and O(2), 2.626(3) Å, is far less than the sum of the van der Waals radii (3.2 Å) suggesting that there may be weak interaction between these two atoms in the solid state. However, the sum of the bond angles, 355.66° supports trigonal planar geometry at Ag(1) and a slight deformation of the geometry due to Ag··O close contact. The Ga−S distances in **3** fall in the range 2.271(2)−2.309(2) Å which are comparable to the Ga−S distances observed in $[Et_3NH][Ga(SC\{O\}Ph)_4]$.[36] The Ag(1)−P(1) and Ag(1)−P(2) distances, 2.451(2) and 2.455(2) Å, respectively, are comparable to those observed in **5**.[28] A weak interaction appears to exist between Ga(1) and O(2) (2.626(4) Å) which is significantly lower than the sum of the van der Waals radii of 3.4 Å.

Table 5. Pyrolysis and TGA Results for 1−5

compd	TG results: temp range (°C)	TG results: residual wt obsd (calcd) (%)	residual wt from pyrolysis[a] (%)	product of decomposition
1	150−327	25.5 (20.9)	20.8	$CuGaS_2$[b]
2	168−350	24.3 (24.5)	24.0	$CuInS_2$[c]
3	185−349	18.9 (19.3)	19.3	$AgGaS_2$[d]
4	132−315	28.4 (27.4)	27.9	$AgInS_2$[e]
5	175−328	23.6 (22.1)	22.1	$AgInS_2$[e]

[a] The samples were heated at 300 °C under a 0.5 Torr pressure for 30 min. [b] Tetragonal $CuGaS_2$ (JCPDS Code 06-0358). [c] Tetragonal $CuInS_2$ (JCPDS Code 27-0159); [d] Tetragonal $AgGaS_2$ (JCPDS 27-0615). [e] Orthorhombic $AgInS_2$ (JCPDS Code 25-1328).

The structures of **1** and **2** exhibit subtle differences in the bonding modes of the thiocarboxylate anion. In **1**, μ_2-*S*,*O* and μ_2-*S* bonding modes are displayed, whereas in **2**, μ_2-*S*,*O* and μ_2-S_2,*O* are observed. These changes in bonding modes may be attributed to the change in the size of the metal atoms. The bimetallic compounds of Ag and Ga/In show interesting structural features. In **3**, the metal atoms Ag and Ga are bridged by a thiobenzoate anion through a μ_2-*S* bonding while another thiobenzoate ligand bonded to the gallium metal atom weakly interacts with the silver metal atom through its oxygen donor site. On the other hand, the Ag and In metal centers are bridged by two $PhC\{O\}S^-$ ligands in **5**.[28] Furthermore, the Cu−Ga and Cu−In distances in **1** and **2**, respectively, are shorter than the sums of their van der Waals radii, while the Ag−In distance in **5** is not. The soft Cu atom is always bonded to the soft S donor sites; the harder Ga atoms accept S and O donor centers but its site does allow a coordination number of four in these compounds. The larger In atom achieves a coordination number of six by bonding the thiocarboxylate ions in a chelating mode.

Thermogravimetric and Pyrolysis Studies. The usefulness of **1**−**5** as single-source precursors for ternary sulfide materials was investigated by thermogravimetry and pyrolysis experiments. The TG curves are presented in Figure 4 and the results are tabulated in Table 5. The loss of dichloromethane in **2** was observed in the temperature range 79−111 °C. The observed weight loss, 6.3%, matched well with the calculated value, 6.4%, for the loss of a half molecule of CH_2Cl_2. It is unusual that CH_2Cl_2 is lost at such a high temperature. The elemental analysis of **2** also indicated the presence of half a CH_2Cl_2 molecule per formula unit. This suggests that the CH_2Cl_2 molecules are strongly occluded in **2**. The TG experiment on solvent-free **2** confirmed that the initial weight loss is indeed due to the loss of CH_2Cl_2.

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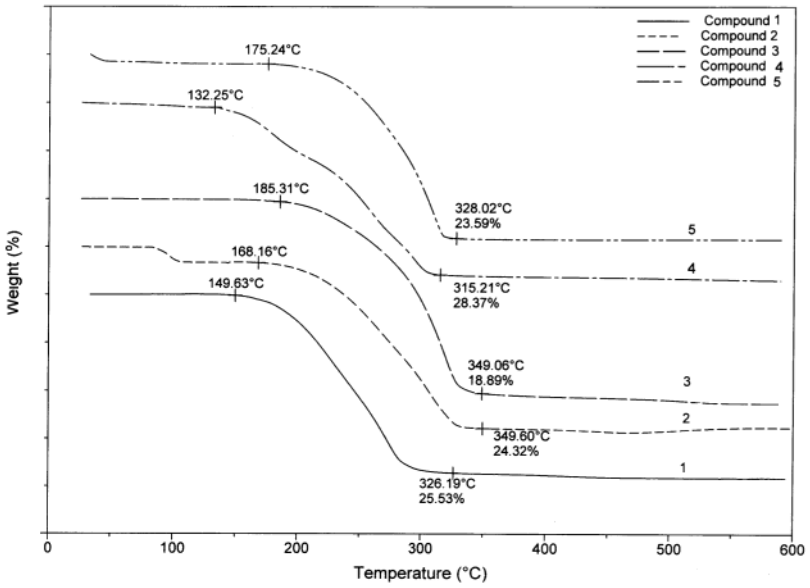

Figure 4. Thermogravimetric curves of **1**−**5**.

TG data reveal that the compounds decompose in the temperature range 150−350 °C in unresolved multiple steps to stable final products, which were found to be the corresponding ternary sulfides. The residual masses for **1**−**5** agree with the formation of the ternary sulfides except for **1** as shown in Table 4. The residue of **1** probably contains some side products of decomposition. On the basis of the thermal decomposition pathway of metal thiocarboxylates discussed by Hampden-Smith[37−41] the decomposition reaction may be described as in eq 4.

$$[(Ph_3P)_xMM'(SC\{O\}R)_4] \rightarrow MM'S_2 + 2RC(O)SC(O)R + xPPh_3 \quad (4)$$

To identify the nature of the ternary materials obtained, all compounds were subjected to pyrolysis at 300 °C at a pressure of 0.5 Torr for 30 min. The ternary materials thus obtained were characterized by X-ray powder diffraction, EDAX, and SEM. The XRPD patterns are shown in Figure 5. The residues obtained from **1** and **2** matched the tetragonal phases of $CuGaS_2$ and $CuInS_2$ (JCPDS database). Pyrolysis of **3** resulted in formation of tetragonal $AgGaS_2$. The X-ray powder diffraction patterns of these residues suggested a high degree of crystallinity. The EDAX profiles of the samples show peaks for all the corresponding elements, as well as peaks for carbon, due to incorporated graphite mesh and oxygen due to aerobic conditions. The copper/gallium/sulfur and copper/indium/sulfur ratios were found to be 1:1.12:1.82 and 1:1.08:1.89, respectively, confirming the stoichiometry of these compounds. The SEM images (Supporting Information) of the ternary materials showed a wide distribution of particle sizes

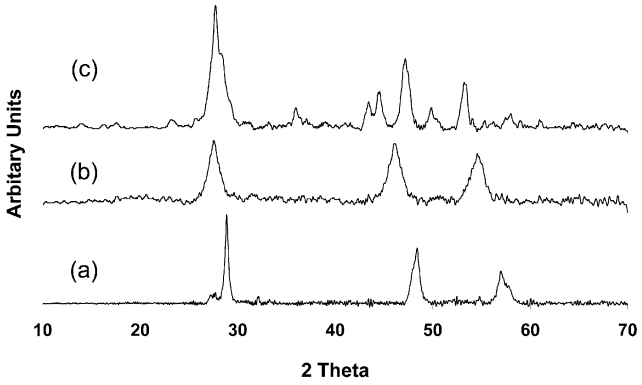

Figure 5. X-ray powder diffraction patterns of (a) $CuGaS_2$ from **1**, (b) $CuInS_2$ from **2**, and (c) $AgGaS_2$ from **3** by pyrolysis.

for the sulfide materials which account for the broad peaks observed in their X-ray powder diffraction patterns. The particle size of the sulfide materials ranges from 5 to 50 μm.

Aerosol-Assisted Chemical Vapor Deposition of [(Ph$_3$P)Cu(SC{O}Ph)$_3$In(SC{O}Ph)]. Attempts to deposit thin films using **2** as a single-source precursor by aerosol-assisted chemical vapor deposition resulted in predominantly β-In_2S_3 materials rather than the expected $CuInS_2$, as was observed from TGA and pyrolysis studies. In most cases, dark yellow β-In_2S_3 films were obtained at growth temperatures of 350−450 °C after 2 h of growth confirmed by XRPD. There were no differences on using different solvents such as THF or toluene. Figure 6 indicates the XRPD pattern of β-In_2S_3 film grown on glass from **2** in toluene at 450 °C after 2 h growth. Broad peaks indicate that crystallinity of the particles is relatively poor and a preferred orientation along the (311) plane is found. Nomura et al. reported the growth of $CuIn_5S_8$ films from BuIn(S^{n}Pr)Cu($S_2CN^nPr_2$) by LP-MOCVD.[42] In their study, a higher growth temperature (450 °C) resulted in films of β-In_2S_3, whereas at lower growth temperatures the films consisted of $CuIn_5S_8$.

XPS was employed to determine photoelectron binding energies of the elements comprising the films grown

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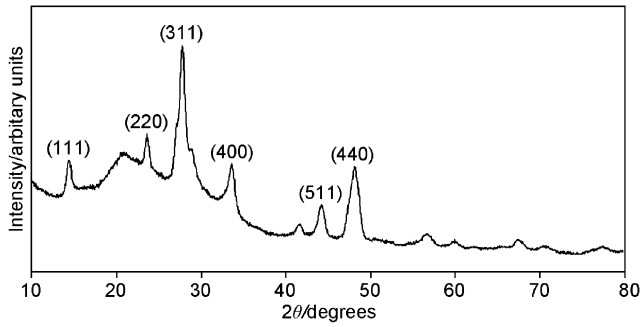


Figure 6. XRPD pattern of a β-In_2S_3 film grown from a solution of compound **2** in toluene at 450 °C by AACVD.

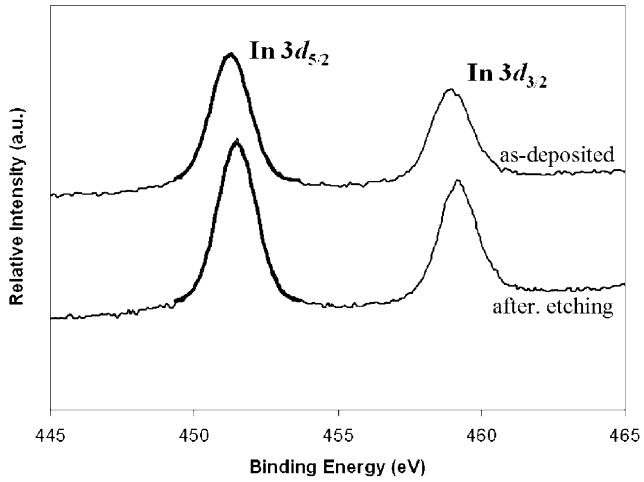


Figure 7. XPS spectra of In 3*d* peaks of a β-In_2S_3 film as-deposited and after 1 h of etching.

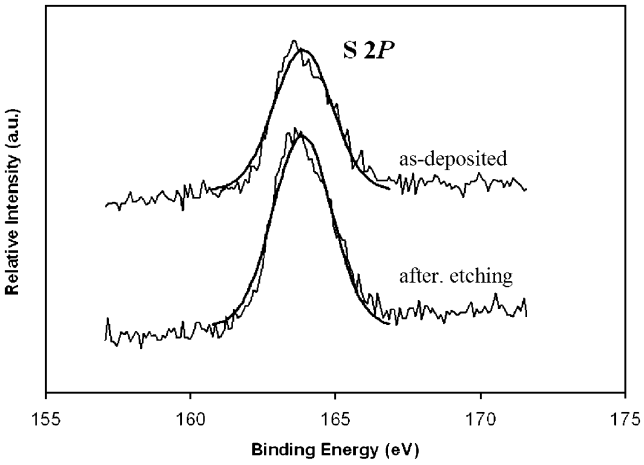
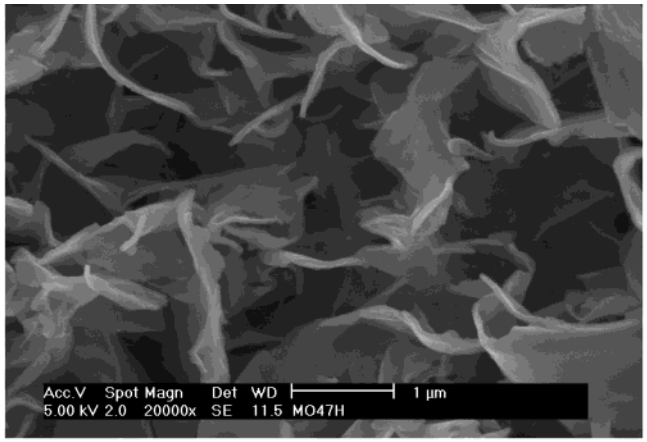
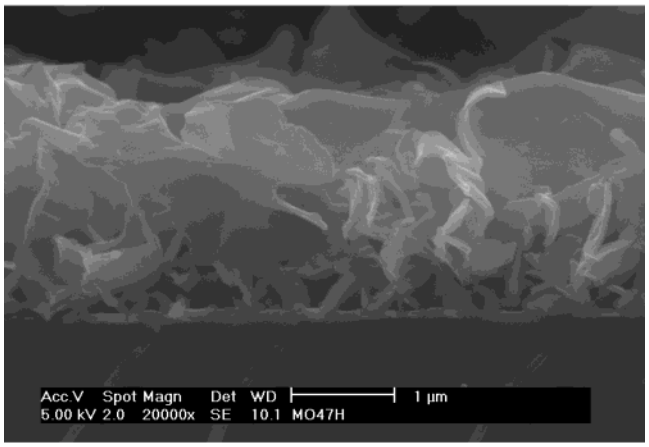


Figure 8. XPS spectra of S 2*s* peaks of a β-In_2S_3 film as-deposited and after 1 h of etching.

from **2** in toluene at 450 °C after 2 h growth. Figures 7 and 8 show In 3*d* and S 2*p* peaks observed before etching and after 1 h of etching. The peaks obtained before and after etching are not significantly different in terms of their binding energies and intensities. Indium 3*d* peaks were found at 451.5 eV (In $3d_{5/2}$) and 458.6 eV (In $3d_{3/2}$) before etching and 451.3 eV (In $3d_{5/2}$) and 458.2 eV (In $3d_{3/2}$) after etching. Sulfur 2*p* peaks were found at 163.9 eV in both cases. Relative atomic



(a)



(b)

Figure 9. SEM images of a In_2S_3 film grown from the solution of toluene and compound **2** at 450 °C: (a) top view, (b) cross-section view.

percentages of indium and sulfur were found to be slightly variable depending on etching treatment (2:3.66 before etching and 2:3.29 after etching).

SEM studies on the In_2S_3 films show that the particles are randomly oriented on the glass substrate (Figure 9) with ca. 1.5 μm/h growth rate. There was also no evidence for copper peaks in the EDAX spectra but in some cases small traces of copper were observed (ca. <1%). This observation suggests that there was a pre-reaction between the precursor and the solvents used in this study during the CVD process. ESI-MS of **2** showed no molecular ion peak, however, signals due to $[In(SC\{O\}Ph)_4]^-$, $[(PPh_3)_2Cu]^+$, and $[(PPh_3)_3Cu]^+$ were present. This indicates the dissociation of the compound in the solution. Such processes are common among phosphine adducts of coinage metal salts and have been substantiated by various techniques including NMR, molecular weight determinations, and conductivity measurements.[43−46] Our finding of dissociation, using

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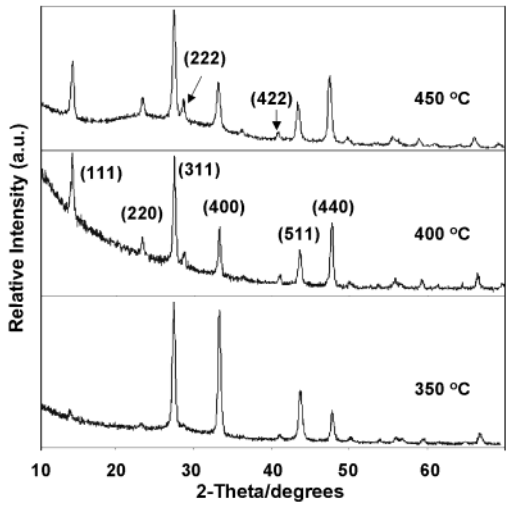

Figure 10. X-ray powder diffraction pattern of $AgIn_5S_8$ thin films formed from **4**.

ESIMS, also concurs with the findings of Henderson et al.[47]

Aerosol-Assisted Chemical Vapor Deposition of [(Ph$_3$P)$_2$Ag(SC{O}R)$_3$In(SC{O}R)] (R = Me (4); Ph (5)). Aerosol-assisted chemical vapor deposition (AACVD) of THF solution of **4** and **5** yielded $AgIn_5S_8$ films. Films grown on glass at 350, 400, and 450 °C from **4** were transparent and adherent (Scotch tape test) with a dark red color, and films grown at 350 °C were slightly red. XRPD analysis (step size 0.04°/2 s) confirmed that the films prepared from compounds **4** and **5** were found to be cubic-$AgIn_5S_8$ (JCPDS 25-1329) with a preferred orientation along the (311) plane (Figure 10). XRPD patterns of films grown from 4 showed the (111) and (222) planes were noticeably enhanced with increasing growth temperature, and intensities of peaks from the (511) and (440) planes were also reversed. XRPD measurements of films from compound **5** indicate similar patterns but no indication of enhancement of peak intensities was observed in the case of the films grown from **4**.

Scanning electron microscopy (SEM) images (Figure 11) of the $AgIn_5S_8$ films obtained from **4** show the dramatic changes in the morphology of films grown as a function of growth temperatures. The morphology of the films grown on glass at 450 °C (Figure 11c) consists of thin platelike particles, positioned laid down onto the substrate with random orientation, and a similar morphology was also found in the films grown on Si(100) substrates at the same temperature. However, with decreasing the growth temperature to 400 or 350 °C, the morphology becomes more dense and no platelike particles were formed (Figure 11a and b). Growth rate and average particle size of the films grown at 400 °C were ca. 0.3 μm/h and ca. 0.5 μm, respectively, and at 350 °C were ca. 0.2 μm/h and ca. 0.3 μm.

Morphologies of films grown from compound **5** (Figure 12) are quite different from those grown from **4**. Films obtained at a growth temperature of 350 °C revealed a relatively dense morphology and a smaller particle size (ca. 100−300 nm) than those prepared from higher growth temperatures. Particles on glass substrates (Figure 12c) grown at 450 °C have trigonal habits consisting of several layers. However, on changing the substrate from glass to Si(100), the formation of par-

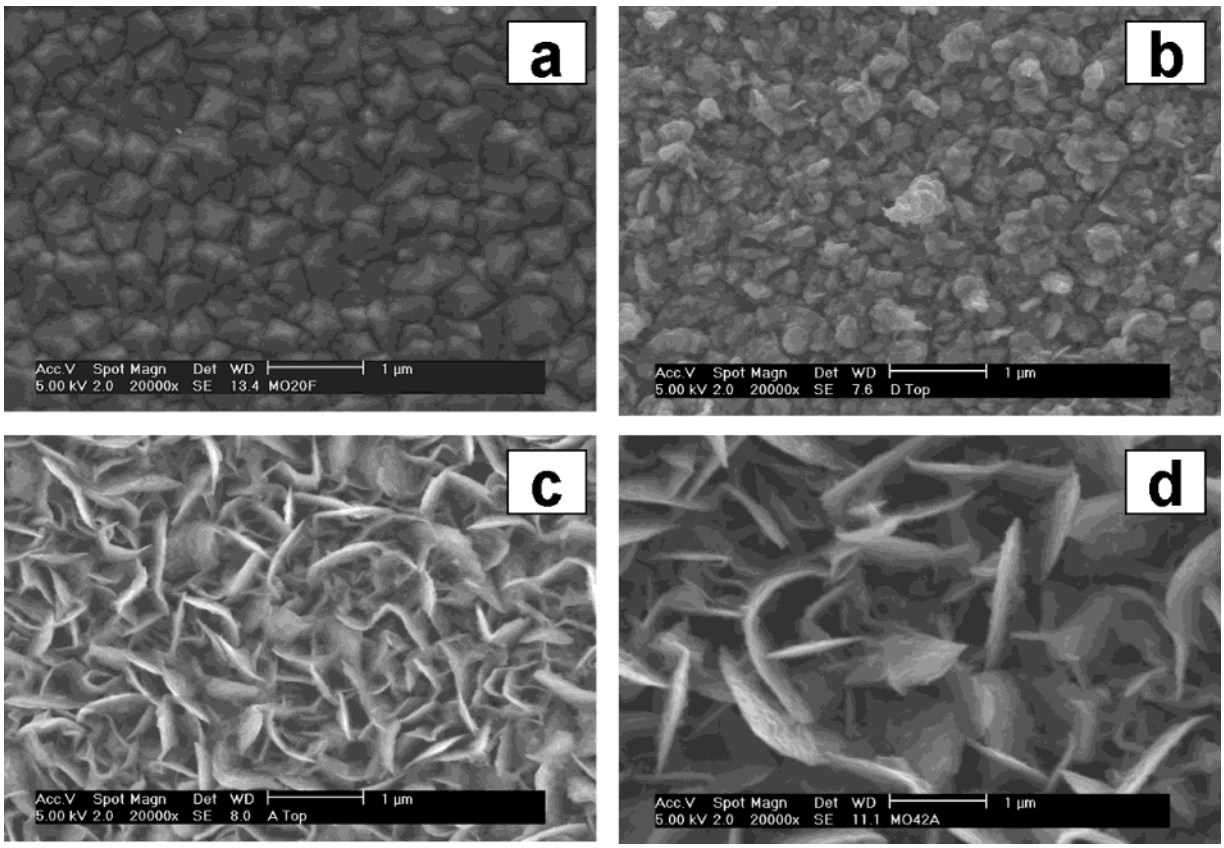

Figure 11. SEM images of $AgIn_5S_8$ films on glass grown from **4**: (a) 350 °C on glass, (b) 400 °C on glass, (c) 450 °C on glass, and (d) 450 °C on Si(100).

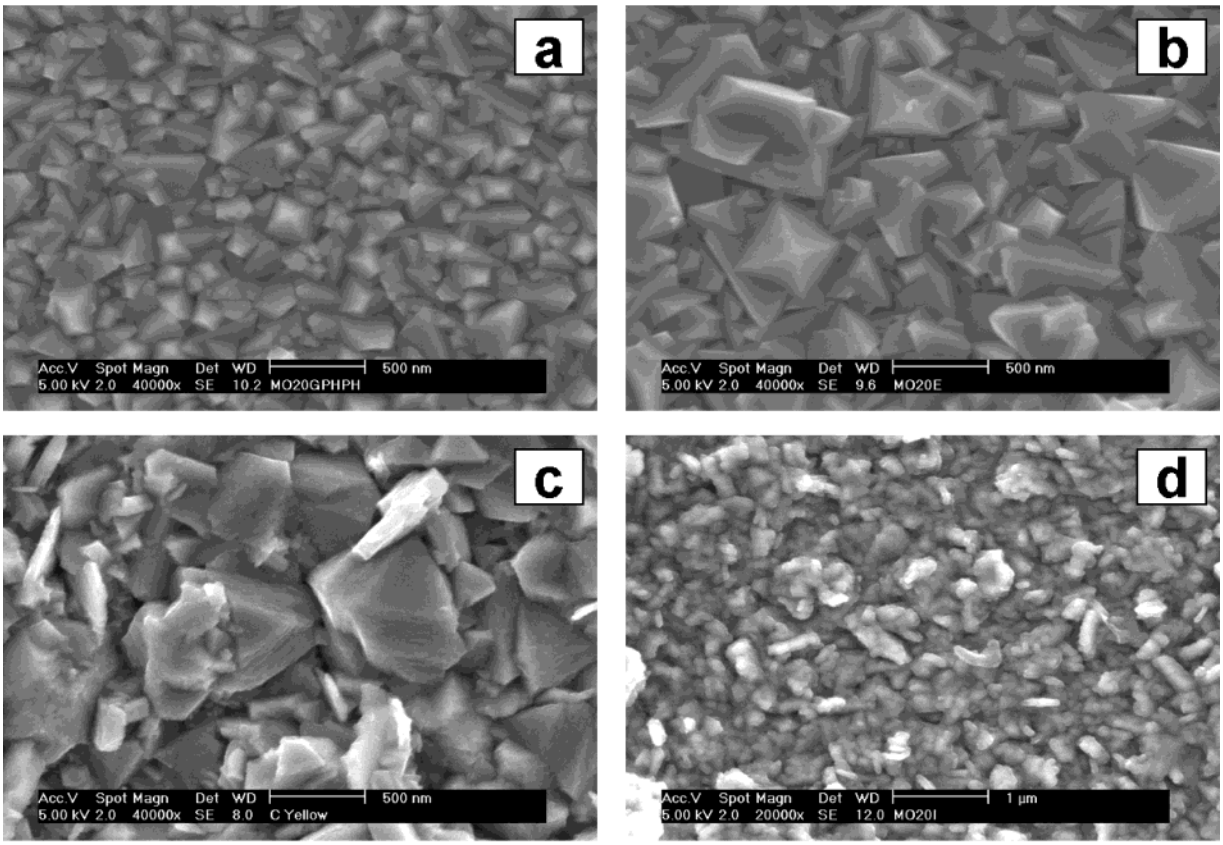

Figure 12. SEM images of $AgIn_5S_8$ films on glass grown from **5**: (a) 350 °C on glass, (b) 400 °C on glass, (c) 450 °C on glass, and (d) 450 °C on Si(100).

ticles leads to rice-like instead of triangular shapes (Figure 12d). Growth rates obtained from cross-section views for the films were found to be ca. 0.2 μm/h at 350 °C, 0.5 μm/h at 400 °C, and 0.6 μm/h at 450 °C on glass substrates after 2 h of growth.

Conclusion

In this paper, we have reported the syntheses and characterization of the compounds $[(Ph_3P)CuM(SC\{O\}Ph)_4]$ (M = Ga (**1**) or In (**2**)) and $[(Ph_3P)_2AgGa(SC\{O\}Ph)_4]$ (**3**). The structures of the three compounds have been determined by X-ray crystallography. Thermogravimetric analyses and pyrolysis studies of **1**−**5** indicate that these compounds decompose to give ternary $MM'S_2$ materials. Compounds **4** and **5** can also be used as precursors for $AgIn_5S_8$ films as was demonstrated by AACVD experiments. These compounds may also have the potential to be used to prepare nanocrystalline sulfides via the single-source molecular precursor route.

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Supporting Information Available: SEM micrographs of the pyrolysis products of compounds **1**−**5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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