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Deposition of tetragonal β-In_2S_3 thin films from tris(N,N-diisopropylmonothiocarbamato)indium(III), $In(SOCN^iPr_2)_3$, by low pressure metal–organic chemical vapour deposition

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Tris(N,N-diisopropylmonothiocarbamato)indium(III), $In(SOCN^iPr_2)_3$, has been prepared by the reaction of indium(III) chloride and lithium N,N-diisopropylmonothiocarbamate. In the solid state, the complex is a distorted trigonal prismatic monomer with a meridional configuration, as characterised by single-crystal X-ray diffraction. $In(SOCN^iPr_2)_3$ has been used as a single-source precursor for the deposition of tetragonal β-In_2S_3 thin films by low pressure metal–organic chemical vapour deposition (LP-MOCVD) at temperatures ranging from 300 to 450 °C, on borosilicate glass substrates.

Introduction

There has been recent interest in the preparation of group 13 chalcogenide materials. In particular thin films of the type ME or M_2E_3 (M = Al, Ga, In, Tl; E = S, Se, Te) have been shown to have attractive properties for a number of optical and electronic applications.[1,2] Indium sulfide is a mid band-gap semiconductor which, as is typical for the group 13 chalcogenides, shows a number of forms [*i.e.* InS ($E_g = 2.44$ eV) and β-In_2S_3 ($E_g = 2.07$ eV)].[3,4] A number of techniques have been utilised to deposit such materials, although by far the most commonly studied growth technique is metal–organic chemical vapour deposition (MOCVD), either at low or atmospheric pressure (LP- or AP-MOCVD), or related methods such as aerosol-assisted (AACVD), or plasma-enhanced (PECVD) chemical vapour deposition.

Single-source precursors have often been used for the deposition of group 13 chalcogenide thin films (*i.e.* both the metal and chalcogen atoms are contained within the precursor complex); a number of different chalcogen containing ligands have been employed for the preparation of such precursor complexes, including thiolates,[5,6] selenolates,[7] thiocarboxylates,[8] thiocarbonates,[9] dithiocarbamates[10,11] and diselenocarbamates.[12]

Recently, we have reported the preparation of thin films of the cubic β-phase of indium sulfide (β-In_2S_3) from the novel monothiocarbamato precursor, $In(SOCNEt_2)_3$, as deposited on glass substrates at 350 to 500 °C, by LP-MOCVD.[13] Subsequently, we have also developed the growth of cubic gallium sulfide (GaS) from the analogous gallium complex, $Ga(SOCNEt_2)_3$, by AACVD.[14] Here, we continue our investigations into monothiocarbamato systems and report the deposition of indium sulfide thin films from the related diisopropylmonothiocarbamato complex, $In(SOCN^iPr_2)_3$, on borosilicate glass substrates by LP-MOCVD.

Experimental

Indium(III) chloride was a gift from Epichem Ltd. Toluene (BDH) was distilled over Na–benzophenone and degassed prior to use. Carbonyl sulfide and lithium diisopropylamide (Aldrich) were used as purchased. All manipulations and reactions were carried out in an inert atmosphere using Schlenk techniques and a vacuum line. Low-pressure growth experiments ($\approx 10^{-2}$ Torr) were carried out using an Edwards model E2M8 vacuum pump system and the films were deposited on borosilicate glass substrates by LP-MOCVD. Growth experiments were carried out using a cold wall reactor, which has been described elsewhere.[15]

Preparation of tris(N,N-diisopropylmonothiocarbamato)indium(III), $In(SOCN^iPr_2)_3$

(i) Preparation of $Li^+(SOCN^iPr_2)^-$. Lithium diisopropylamide solution (2.0 M in tetrahydrofuran–ethylbenzene –heptane, 4.0 ml, 8.0 mmol) was placed in a flask with dry tetrahydrofuran (*ca.* 30 ml). Carbonyl sulfide was bubbled through the solution, until heat evolvution from the ensuing reaction was no longer detected (*ca.* 2 h). Reaction was accompanied by an increased viscosity of the solution, and a colour change from brown to yellow. All volatile components were removed *in vacuo* to yield an orange oil, which was used as collected [62% yield based on $LiN(C_3H_7)_2$].

(ii) Preparation of $In(SOCN^iPr_2)_3$. Lithium diisopropylmonothiocarbamate (0.53 g, 4.95 mmol) was dissolved in dry toluene (*ca.* 20 ml) and added to a suspension of indium(III) chloride (0.48 g, 1.65 mmol) in dry toluene (*ca.* 10 ml). Heat was evolved initially, and a light yellow solution was obtained after stirring for 3 h. The solvent was removed *in vacuo* to yield a creamy-white solid. Recrystallisation from toluene gave colourless, rhombohedral crystals (76% yield based on $InCl_3$). ^1H NMR (C_6D_6, 400 MHz): δ 0.72 (6H, d, CH_3, $^3J_{HH}$ 6.8 Hz), 0.94 (1H, m, CH), 1.27 (6H, d, CH_3, $^3J_{HH}$ 6.8 Hz), 1.45 (1H, m, CH). ^{13}C NMR (C_6D_6, 100 MHz): δ 19.75 (CH_3), 20.60 (CH_3), 47.16 (NC), 47.40 (NC), 181.79 (NCOS). IR (Nujol mull): 629, 677, 723, 834, 876, 921, 1037, 1102, 1150, 1210, 1358, 1462, 1546, 2854, 2926, 2954 cm^{-1}. Microanalysis: Calc. for $C_{21}H_{42}N_3O_3S_3In$: C, 42.34; H, 7.11; N, 7.05. Found: C, 41.91; H, 6.77; N, 7.12%).

Physical measurements

NMR spectra were recorded using a Bruker AM400 pulsed Fourier-transform spectrometer. IR spectra were recorded on a Mattson Polaris FTIR spectrometer as Nujol mulls between potassium bromide plates. X-Ray powder diffraction analysis was performed by a Philips PW1700 series automated diffractometer. Samples were mounted flat, and scanned from 10–60° in steps of 0.04°, with a count time of 2 s. Electron

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microscopy and energy dispersive analytical X-ray analysis (EDAX) was carried out on JEOL J535CM and JEOL T220-A scanning electron microscopes with a LINK QX2000 energy dispersive X-ray analysis unit. Microanalyses were carried out by the service at Imperial College. Melting points were recorded in sealed tubes with an electrothermal melting point apparatus.

Single-crystal X-ray diffraction study

Crystal data for In(SOCN^{i}Pr$_2$)$_3$: $C_{21}H_{42}N_3O_3S_3In$, $M = 595.6$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.716(2)$, $b = 12.652(2)$, $c = 12.832(4)$ Å, $\alpha = 89.17(2)$, $\beta = 66.16(2)$, $\gamma = 66.03(1)°$, $V = 1430.7(5)$ Å^3, $Z = 2$, $D_c = 1.382$ g cm^{-3}, μ(Mo-Kα) = 10.7 cm^{-1}, $F(000) = 620$, $T = 183$ K; monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å, ω-scans, 5026 independent reflections. Structure was solved by direct methods, non-hydrogen atoms refined anisotropically by full matrix least squares based on F^2 to give $R_1 = 0.042$, $wR_2 = 0.094$ for 4138 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 50°$] and 281 parameters. All computations were carried out using the SHELXTL PC program system.[16]

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/151.

See http://www.rsc.org/suppdata/jmc/1999/1289/ for crystallographic files in .cif format.

Results and discussion

The new complex, tris(*N*,*N*-diisopropylmonothiocarbamato)-indium(III), In(SOCN^{i}Pr$_2$)$_3$, was prepared by the reaction of as-prepared lithium diisopropylmonothiocarbamate with a stoichiometric quantity of indium(III) chloride. This preparation differs from that used in the synthesis of In(SOCNEt$_2$)$_3$,[13] in that a sodium diethylmonothiocarbamate salt was prepared from a diethylammonium salt [Et$_2$NH$^+$(SOCNEt$_2$)$^-$], prepared by the reaction of COS and the secondary amine. The COS insertion route was used in this study, as the diisopropylammonium salt, [^{i}Pr$_2$NH$^+$(SOCN^{i}Pr$_2$)$^-$] formed from the reaction of COS and ^{i}Pr$_2$NH was extremely unstable, and proved difficult to react with sodium hydride. The present route should be applicable to all dialkyl species, and may facilitate a better preparation of asymmetric monothiocarbamate complexes.

In(SOCN^{i}Pr$_2$)$_3$ was recrystallised from toluene to give colourless rhombohedral crystals. The complex is sparingly soluble in most organic solvents, and showed no tendency to decompose when left in air for an extended time period.

Single-crystal X-ray structure of In(SOCN^{i}Pr$_2$)$_3$

The X-ray analysis of In(SOCN^{i}Pr$_2$)$_3$ (Fig. 1) reveals a structure very similar to that of the closely related In(SOCNEt$_2$)$_3$.[13] The geometry at indium is distorted trigonal prismatic, with the co-ordination planes of the chelating monothiocarbamate ligands being inclined at 70, 68 and 89° to the C(1)/C(2)/C(3) plane. Ignoring the peripheral isopropyl groups, the complex has approximate C_s symmetry about a plane including In, S(3), C(3) and O(3). In common with the ethyl analogue, the monothiocarbamate ligands are disposed in a meridional fashion about the metal centre. The probable reason for the adoption of a *mer* rather than a *fac* geometry has been discussed previously.[13]

There is a marked asymmetry in the pattern of bonding to the indium with the In–S and In–O bond lengths to the two ligands 'related' by the molecular mirror plane being very similar [In–S(1) 2.503(2), In–S(2) 2.504(2), In–O(1) 2.295(3), In–O(2) 2.274(3) Å], whereas those to the 'in-plane' ligand are distinctly different; the In–O distance is dramatically longer at 2.355(3) Å and that to the sulfur atom is slightly reduced at 2.481(2) Å. The reason for this asymmetry is not immediately apparent, but it extends to include the C–S and C–O bonds, with the C(3)–S(3) bond being lengthened and the C(3)–O(3) bond shortened relative to the values in the other two ligands (see Table 1); these differences, however, are only at the margin of significance.

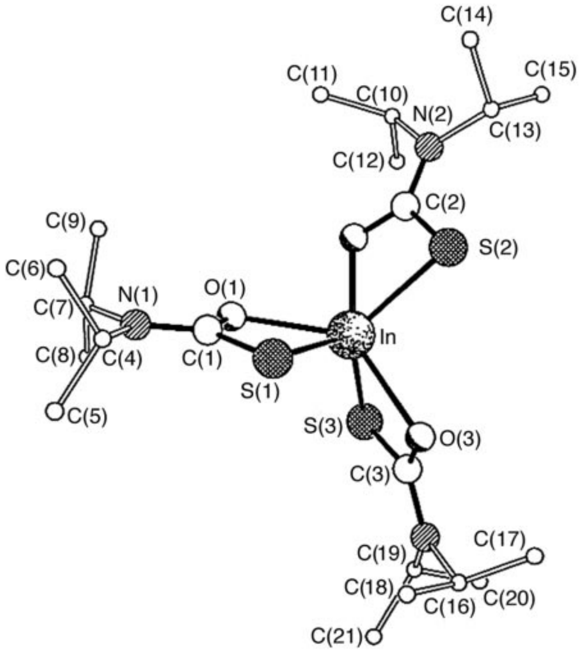

Fig. 1 X-Ray single-crystal structure of In(SOCN^{i}Pr$_2$)$_3$.

Deposition of thin films

Thin films of indium sulfide have been grown using In(SOCN^{i}Pr$_2$)$_3$ as a single source precursor. Deposition was attempted over a range of substrate temperatures (Table 2), with *ca.* 200 mg of the precursor used for each experiment. The films obtained were orange to red in colour, well adhered

Table 1 Selected bond lengths (Å) and angles (°) for In(SOCN^{i}Pr$_2$)$_3$

In–O(2)	2.274(3)	In–O(3)	2.355(3)
In–O(1)	2.295(3)	In–S(1)	2.503(2)
In–S(3)	2.481(2)	In–S(2)	2.504(2)
S(1)–C(1)	1.754(4)	S(2)–C(2)	1.761(4)
S(3)–C(3)	1.772(4)	O(1)–C(1)	1.262(5)
O(2)–C(2)	1.262(5)	O(3)–C(3)	1.253(5)
C(1)–N(1)	1.339(5)	C(2)–N(2)	1.334(5)
C(3)–N(3)	1.336(5)		
O(2)–In–O(3)	141.8(1)	O(2)–In–O(1)	80.8(1)
O(3)–In–O(1)	133.2(1)	O(2)–In–S(1)	127.92(9)
O(3)–In–S(1)	122.05(4)	O(1)–In–S(1)	65.06(8)
O(2)–In–S(3)	99.22(9)	O(3)–In–S(3)	64.76(8)
O(1)–In–S(3)	97.06(8)	S(1)–In–S(3)	122.05(4)
O(2)–In–S(2)	65.17(8)	O(3)–In–S(2)	93.40(8)
O(1)–In–S(2)	130.13(8)	S(1)–In–S(2)	108.24(4)
S(3)–In–S(2)	122.56(4)		

Table 2 Experimental details for the growth of indium sulfide from In(SOCN^{i}Pr$_2$)$_3$

Phase	Growth Temp./°C	Comments
Amorphous	300	Shiny orange crystalline film
β-In$_2$S$_3$	350	Orange crystalline film
β-In$_2$S$_3$	400	Orange–red crystalline film
β-In$_2$S$_3$	450	Near-red crystalline film

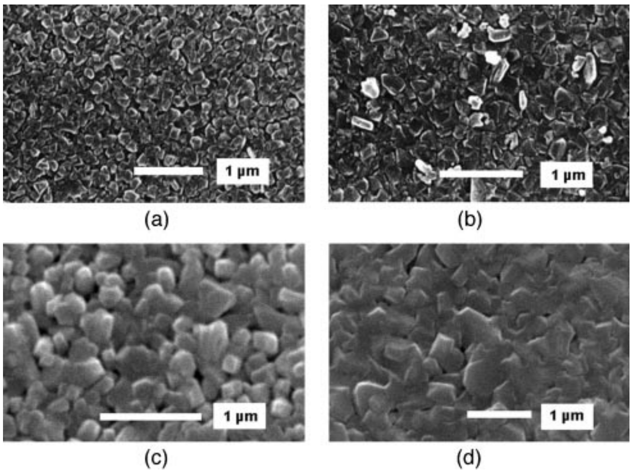

Fig. 2 SEM images of β-In_2S_3 films deposited from In(SOCN^{i}Pr$_2$)$_3$ at (a) 300 °C, (b) 350 °C, (c) 400 °C and (d) 450 °C on glass substrates (note: amorphous at 300 °C).

to the glass substrate surface (Scotch tape test) but could be removed by scratching the surface with a scalpel.

Polycrystalline indium sulfide films were grown from In(SOCN^{i}Pr$_2$)$_3$ at temperatures as low as 350 °C. In contrast, films deposited from In(SOCNEt$_2$)$_3$ at this temperature had poor morphology even after several hours growth.[13] In addition, the rate of deposition of good quality films of indium sulfide is greatly reduced using In(SOCN^{i}Pr$_2$)$_3$ [*ca.* 30 min, compared to 2 h for In(SOCNEt$_2$)$_3$]. At higher deposition temperatures, the degree of crystallinity of the as-deposited films improved, and the particle size also increased. Fig. 2 shows SEM images of the crystalline indium sulfide films deposited from In(SOCN^{i}Pr$_2$)$_3$ at various temperatures.

In(SOCN^{i}Pr$_2$)$_3$ was also found to be to be a more volatile precursor than its diethyl-substituted analogue, In(SOCNEt$_2$)$_3$.[13] This fact may be attributed to increased steric effects associated with the larger alkyl groups which may act to reduce intermolecular interaction. There is a small decrease in the In–S bond distances, and a corresponding increase in the C–O bond length. The increased strain in the delocalised region may enhance deposition as compared to the diethyl compound. The stronger indium–sulfur interactions suggest that increasing the steric bulk of the monothiocarbamate ligand can also improve/change the characteristics of the precursor. Other precursor systems, notably for the dithiocarbamato complexes[11] have improved properties with bulkier substituents. EDAX analysis of the as-deposited films shows the presence of only indium and sulfur. Although the EDAX results are not quantitative, the intensity of the peaks indicated that the indium : sulfur ratio was close to 2 : 3.

Indium sulfide films obtained from In(SOCN^{i}Pr$_2$)$_3$ were analysed by X-ray powder diffraction (XRD) which indicated that the tetragonal β-In_2S_3 phase (JCPDS#: 25-390) had been deposited (Fig. 3). The XRD patterns of the films grown at 350–450 °C showed a preferred orientation along the (109) plane (Table 3). Nomura *et al.* have also reported the deposition of β-In_2S_3, from a dithiolate complex, [^{n}BuIn(S^{i}Pr)$_2$]$_2$, with an indium : sulfur ratio of 1 : 2.[6] Their films grown at 400 °C showed a preferred orientation in the (103) plane. It is suggested that at higher temperatures the decrease in sulfur content of the indium sulfide layers is due to the dissociation of a thiolate moiety from the precursor, resulting in the deposition of an indium-rich film (In_6S_7). In contrast to In(SOCN^{i}Pr$_2$)$_3$ only a single phase (β-In_2S_3) is observed.

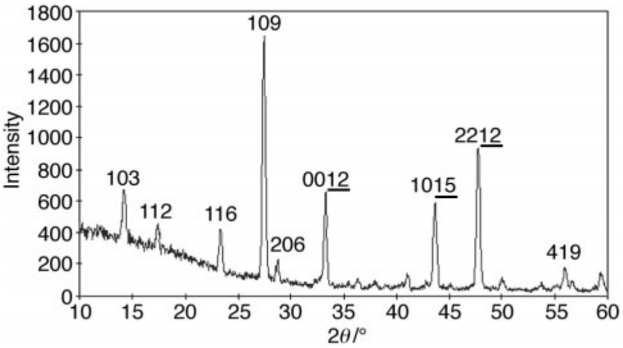

Fig. 3 XRD pattern of the β-In_2S_3 film deposited from In(SOCN^{i}Pr$_2$)$_3$ at 450 °C on glass.

Table 3 X-Ray diffraction data, indices (*hkl*) and *d*-values, for β-In_2S_3 films deposited in these studies (*I* = intensity)

	JCPDS 25–390	β-In_2S_3 (350 °C)	β-In_2S_3 (400 °C)	β-In_2S_3 (450 °C)
hkl	*d*/Å *I* (%)	*d*/Å *I* (%)	*d*/Å *I* (%)	*d*/Å *I* (%)
103	6.210 (30)	6.219 (38)	6.227 (14)	6.221 (21)
112	5.110 (12)	5.029 (2)	5.108 (10)	5.103 (9)
116	3.811 (18)	3.809 (20)	3.804 (21)	3.807 (17)
109	3.249 (100)	3.246 (100)	3.245 (100)	3.246 (100)
206	3.112 (12)	3.107 (10)	3.107 (5)	3.105 (9)
00*12*	2.694 (50)	2.695 (40)	2.690 (38)	2.691 (39)
10*15*	2.074 (45)	2.072 (33)	2.071 (35)	2.042 (36)
22*12*	1.905 (65)	1.907 (47)	1.902 (10)	1.903 (58)

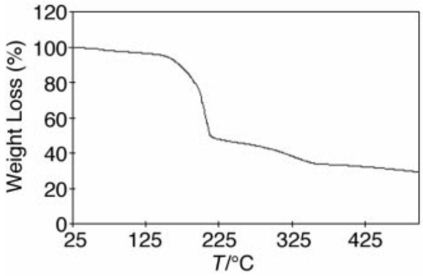

Fig. 4 TGA profile of In(SOCN^{i}Pr$_2$)$_3$ (10 °C min^{-1}).

Thermogravimetric analysis (TGA) of In(SOCN^{i}Pr$_2$)$_3$ (Fig. 4) suggests that the complex decomposes in a two-step mechanism in which two diisopropylmonothiocarbamate ligands dissociate between *ca.* 150 and 220 °C (at 760 Torr). Deposition may well involve an In(S)(SOCN^{i}Pr$_2$) intermediate species that leads to the deposition of only In_2S_3 films at the substrate. The charge distribution in monothiocarbamato complexes ($^-$S–, O=C–) means that the ligands are better sulfiding precursors than might be expected. Furthermore in contrast to Nomura's alkyl based precursors we have a 1 : 3 In : S stoichiometry in the present complex which may lead to better sulfiding of the deposited layer and the consequent predominance of a single (S-rich) phase.

Conclusions

In(SOCN^{i}Pr$_2$)$_3$ has been prepared and characterised by various techniques, and utilised as a single-source precursor for the deposition of tetragonal β-In_2S_3 by LP-MOCVD. The films are well oriented and can be deposited in a relatively short time period (*ca.* 30 min). Analyses of the as-deposited films show that only one phase of indium sulfide is prepared, independent of growth temperature. This is in contrast to some previous studies in this field, where a number of polytypes can be prepared from a single precursor, depending on the substrate temperature.[5,10]

In combination with previous studies,[13] this suggests that monothiocarbamato complexes of group 13 elements are suitable for the deposition of metal chalcogenide materials, with the potential to deposit good quality thin films at relatively low substrate temperatures (*i.e.* <400 °C). Our continuing studies in this area will focus on the preparation of asymmetric monothiocarbamato complexes in an attempt to further reduce deposition temperatures.

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