

Polyhedron 20 (2001) 2989-2995



Organotin unsymmetric dithiocarbamates: synthesis, formation and characterisation of tin(II) sulfide films by atmospheric pressure chemical vapour deposition

A.T. Kana^a, T.G. Hibbert^a, M.F. Mahon^a, K.C. Molloy^{a,*}, I.P. Parkin^b, L.S. Price^b

^a Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK ^b Department of Chemistry, University College London, 20 Gordon Street, London, WC1H OAJ, UK

Received 24 May 2001; accepted 13 August 2001

Abstract

A series of tin unsymmetric dithiocarbamate complexes have been made from metathesis reaction of $[CH_3(C_4H_9)NSC_2]Li$ and R_nSnCl_{4-n} ; $[R_nSn(S_2CN(C_4H_9)CH_3)_{4-n}]$ [n = 3, R = Me (1), Bu (2), Ph (3); n = 2, R = Me (4), Bu (5), Ph (6); n = 1, R = Me (7), Bu (8), Ph (9)]. The complexes were characterised by microanalysis, ¹³C, ¹H and ¹¹⁹Sn NMR, Mössbauer and, in the case of 3, by X-ray diffraction, which revealed one short Sn–S [2.4631(9) Å] and one long Sn–S interaction [3.084(1) Å] indicative of a weakly chelating dithiocarbamate ligand. Atmospheric pressure chemical vapour deposition using 1 and 8 with H₂S at 350–550 °C produced SnS and Sn₂S₃ films on glass substrates. The tin sulfides were analysed by Raman, EDAX, SEM and band gap measurements. Growth rates were of the order of 150 nm min⁻¹. © 2001 Published by Elsevier Science Ltd.

Keywords: Tin; Dithiocarbamates; Thin film; APCVD; X-ray structures

1. Introduction

Tin sulfide has three main phases: SnS and SnS₂ that exhibit layer structures and mixed valence Sn₂S₃ that forms a ribbon structure [1]. Tin(II) sulfide consists of a distorted rock salt structure which is isostructural with germanium sulfide; six sulfur atoms surround each tin atom with three short Sn-S bonds within the layer and three long bonds formed to sulfur atoms in the next layer [2,3]. Tin(II) sulfide has found application as a solid-state lubricant [4,5]. Tin(IV) sulfide is isostructural with CdI₂; each tin atom is octahedral with three sulfur atoms above and below; weak S-S interactions between the SnS_2 sheets [6,7] also make this material a useful lubricant [4,5]. It has in excess of 70 poly-type structures dependent on the overlap of the sulfur-sulfur sheets. Ditin trisulfide is a type I mixed valence Sn(II)/ Sn(IV) compound which has a similar local order to the other tin sulfides, however it exhibits a ribbon structure,

with one tin atom being six coordinate and the other atom three coordinate [8]. All of the tin sulfides show interesting optical spectra and semiconducting properties; SnS₂ has a band gap of 2.07–2.18 eV (depending on exact poly-type) and is an n-type semiconductor [9], Sn_2S_3 is a direct forbidden semiconductor with a band gap of 0.95 eV and has highly anisotropic conduction [10], while SnS can act as either an n-type or p-type conductor (dependent on minor stoichiometry variations) and typically has a band gap of 1.3 eV, although values from 1.08 to 1.51 eV have been reported [11]. All of the tin sulfides have excited interest as semiconductors although SnS has elicited most attention as its electronic band gap of 1.3 eV is midway between silicon and GaAs [12] and as such has potential applications in solar cells and holographic recording media [13,14].

Tin-sulfide thin-films have received scant attention compared to the extensive thin-film technology of silicon and gallium arsenide. Chemical baths have been used to deposit a range of tin sulfide films [15]. A bath containing SnCl₂, Na₂S₂O₃ and EDTA in aqueous solution has been used to deposit SnS on glass and titanium

^{*} Corresponding author. Tel.: +44-1225-826-382; fax: +44-1225-826-231.

E-mail address: chskcm@bath.ac.uk (K.C. Molloy).

substrates [16]. A related solution of SnCl₂, ammonia, thioacetamide and glacial acetic acid has been used to grow SnS films on the sides of suspended glass slides at 75 °C [17]. A dipping method has been used to form tin sulfide films by immersing glass slides into alternate solutions containing Na₂S and SnCl₂ [18]. Tin(IV) sulfides have also been grown by dip-coating [19]. The tin-sulfide films produced from chemical baths showed the presence of significant impurities, are poorly adhesive and required post-treatment to produce a crystalline film [20]. Improved tin sulfide films have been grown at the anode in cyclic voltammetry experiments [21] and from spray-pyrolysis using SnCl₂ and dimethylthiourea [22]. Deposition methods from the gas phase have included limited examples of low pressure [23] and plasma assisted chemical vapour deposition (CVD) [14]. Plasma enhanced CVD reaction of SnCl₄ and H₂S at 100-350 °C produced SnS films on small silica substrates that were contaminated with chlorine and elemental sulfur. Organometallic precursor routes to tin sulfide films on CaF₂ substrates were reported by reaction of tetraalkyltin species with hydrogen sulfide and hydrogen at 600 °C, although the materials were only characterised by thickness measurements and colour. The authors speculated that SnS formed because of the reducing conditions employed in the experiment [23].

We have instituted an intensive study of tin sulfide films on glass substrates by atmospheric pressure and aerosol assisted CVD. Reaction of tin tetrahalides with H₂S under atmospheric pressure chemical vapour deposition (APCVD) conditions provided a facile route to high-quality, phase-pure, uniform, conformal tin sulfides on glass-substrates [24-26]. The tin sulfides deposited in the experiments were directly related to the temperature of the substrate and were largely invariant of the precursor concentration. At 300-500 °C single phase SnS_2 was deposited; at 525 °C Sn_2S_3 formed whilst at 550 °C and above single phase SnS was observed. Growth rates under optimum conditions were in excess of 1 μ m min⁻¹. We have expanded this study to other tin sources and dual-source reactions involving organotin carboxylates [Bu₃SnO₂CCF₃] [27] from which only one phase of tin sulfide, SnS, was produced at 300-550 °C.

The next goal was to produce single-source precursors to tin sulfide coatings. A range of volatile precursors such as $[Sn(SCH_2CF_3)_4]$ and $[Sn(SPh)_4]$ were investigated [28,29]. These homoleptic materials contain an all-sulfur primary co-ordination-sphere and would be expected to form tin sulfides under CVD conditions. This is a precursor strategy that is at the heart of all single-source CVD studies and enshrines a molecular Achilles heel within the molecule that on decomposition in the gas phase will form the required coating by maintaining the metal-element bond. Unfortunately, all of these single source systems failed to deposit tin sulfides in the absence of H_2S . This failure was tracked to a facile disulfide (RS–SR) elimination pathway. Subsequent molecular orbital calculations and an extensive literature search has revealed that the general class of [M(SR)₄] (M = Group IV) molecules suffer significant distortions from tetrahedral geometry because of non-covalently bonded S…S interactions. This distortion and *cis*-annular interaction promotes the disulfide elimination pathway [30]. It should be noted that all of the single source precursors could be made to deposit tin(II) sulfide coatings by employing a minimal flow of H_2S in the system.

In the search for new single-source precursors to tin sulfide films we report here the synthesis, characterisation and APCVD of unsymmetric tin dithiocarbamate derivatives. The dithiocarbamate ligands provide direct Sn–S bonds and would be expected not to undergo an elimination pathway as readily because of the chelate effect. Our interest in the usage of these ligands extends from the extensive work of O'Brien on the deposition of II–VI films [31] where it was noted that unsymmetrical dithiolates are significantly more volatile than the symmetric analogues.

2. Experimental

2.1. General

Manipulations were carried out under an atmosphere of dry N₂. [CH₃(C₄H₉)NSC₂]Li was prepared as described previously [32]. Methylene chloride was dried by distillation over CaH₂. All other solvents and reagents were obtained commercially and used without further purification. All NMR spectra were recorded as saturated CDCl₃ solutions at room temperature on a JEOL 270MHz spectrometer. Chemical shifts are in ppm with respect to Me₄Si (¹H, ¹³C) or Me₄Sn (¹¹⁹Sn); coupling constants in Hz. Details of our Mössbauer spectrometer and related procedures are given elsewhere [33]. Isomer shift (IS), quadrupole splittings (QS) and full width at half height (Γ) are in mm s⁻¹ and were measured at 78 K.

2.2. Synthesis of organotin dithiocarbamates

2.2.1. Generalised route using solid organotin starting materials

The organotin reagent and the appropriate stoichiometric amount of $[CH_3(C_4H_9)NSC_2]Li$ were placed in a dry Schlenk tube against an N₂ counter-flow. CH_2Cl_2 (50 ml) was then added and the reagents were stirred at room temperature for 16 h. LiCl was removed by filtration and the solvent was removed in vacuo. Recrystallisations were from Et₂O.

2.2.2. $[Me_3Sn(S_2CN(CH_3)C_4H_9)]$ (1)

Orange oil, 85% yield, microanalysis (required for C₉H₂₁SN₂Sn): C, 33.3 (33.2); H, 6.5 (6.5); N, 4.3 (4.3); ¹H NMR: 0.59 [9H, s, ²J(^{119,117}SnH) = 57.2, 52.0, SnCH₃], 0.95 (3H, t, J = 7.3, Bu CH₃), 1.35 (2H, m, J = 7.7, CH₂), 1.69 (2H, p, J = 7.0, CH₂), 3.40 (3H, s, NCH₃), 3.87 (2H, t, J = 7.3, NCH₂); ¹³C NMR: 0.6 [SnCH₃, ¹J(^{119,117}SnC) = 382, 366], 15.3 (Bu CH₃), 21.5 (CH₂), 30.5 (CH₂), 44.6 (NCH₃), 58.9 (NCH₂), 198.7 (CN); ¹¹⁹Sn NMR: 22.1; Mössbauer: IS 1.27, QS 2.14, Γ 1.00.

2.2.3. $[Ph_3Sn(S_2CN(CH_3)C_4H_9)]$ (3)

White solid, 93% yield, m.p. 87–88 °C, microanalysis (required for $C_{24}H_{27}NS_2Sn$): C, 56.0 (56.3); H, 5.4 (5.3); N, 2.7 (2.7); ¹H NMR: 0.77 (3H, t, J = 7.2, Bu CH₃), 1.05 (2H, m, J = 7.5, CH₂), 1.32 (2H, m, J = 7.7, CH₂), 2.89 (3H, s, NCH₃), 3.41 (2H, t, J = 7.5, NCH₂), 7.28 (9H, m, ArH), 8.07 (6H, d, J = 7.9, ArH); ¹³C NMR: 14.1 (Bu CH₃), 20.4 (CH₂), 29.4 (CH₂), 43.5 (NCH₃), 58.7 (NCH₂), 129.3 (ArC), 129.7 (ArC), 137.6 (ArC), 148.2 (ArC), 196.5 (CN); ¹¹⁹Sn NMR: – 190.0; Mössbauer: IS 1.23, QS 1.79, Γ 1.05.

2.2.4. $[Me_2Sn(S_2CN(CH_3)C_4H_9)]_2$ (4)

White solid, 89% yield, m.p. 88–89 °C, microanalysis (required for $C_{14}H_{30}N_2S_4Sn$): C, 33.5 (33.5); H, 6.4 (6.4); N, 6.0 (5.9); ¹H NMR: 0.81 (6H, t, J = 7.2, Bu CH_3), 1.11 (4H, m, J = 7.7, CH_2), 1.40 (4H, p, J = 7.5, CH_2), 1.94 [6H, s, ${}^2J({}^{119,117}Sn-H) = 86.4$, 82.8, SnC H_3], 2.98 (6H, s, NC H_3), 3.52 (4H, t, J = 7.7, NC H_2); ¹³C NMR: 14.2 (Bu CH_3), 16.5 (Sn CH_3) 20.4 (CH_2), 29.4 (CH_2), 42.3 (NC H_3), 57.1 (NC H_2), 200.8 (CN); ¹¹⁹Sn – 349.2; Mössbauer: IS 1.40, QS 2.89, Γ 0.90.

2.2.5. $[Ph_2Sn(S_2CN(CH_3)C_4H_9)_2]$ (6)

White solid, 94% yield, m.p. 121–122 °C, microanalysis (required for $C_{24}H_{34}N_2S_4Sn$): C, 48.3 (48.2); H, 5.7 (5.7); N, 4.7 (4.7); ¹H NMR: 0.93 (6H, t, J = 7.3, Bu CH_3), 1.33 (4H, m, J = 7.5, CH_2), 1.68 (4H, m, J = 7.5, CH_2), 3.31 (6H, s, NCH₃), 3.73 (4H, t, J = 7.7, NCH₂), 7.28 (6H, m, J = 7.7, ArH), 8.07 (4H, d, J = 7.7, ArH); ¹³C NMR: 13.7 (Bu CH₃), 19.9 (CH₂), 28.9 (CH₂), 43.3 (NCH₃), 58.3 (NCH₂), 128.1 (ArC), 128.3 (ArC), 134.2 (ArC), 151.7 (ArC), 199.2 (CN); ¹¹⁹Sn – 505.3; Mössbauer: IS 1.26, QS 2.31, Γ 1.20.

2.3. Generalised route using liquid organotin starting materials

 $[CH_3(C_4H_9)NSC_2]Li$ [32] was suspended in CH_2Cl_2 (50 ml) in a Schlenk tube. The appropriate stoichiometric amount of the organotin reagent was then added via syringe and the reagents were stirred at room temperature for 16 h. Nascent LiCl was removed by filtration and the solvent was removed in vacuo. Recrystallisations were from Et_2O .

2.3.1. $[{}^{n}Bu_{3}S([S_{2}CN(CH_{3})C_{4}H_{9})]$ (2)

Yellow oil, 60% yield, microanalysis (required for C₁₈H₃₉NS₂Sn); C, 47.7 (47.8); H, 8.7 (8.7); N, 3.3 (3.1); ¹H NMR: 0.84 (9H, t, J = 7.3, Bu CH₃), 0.88 (3H, t, J = 7.3, Bu CH₃), 1.24 (6H, m, J = 7.3, CH₂), 1.26 (6H, m, J = 7.3, CH_2), 1.29 (2H, m, J = 7.3, CH_2), 1.56 (6H, m, J = 7.5, CH_2), 1.62 (2H, m, J = 9.1, CH_2), 3.34 (3H, s, NCH₃), 3.82 (2H, t, J = 7.7, NCH₂); ¹³C NMR: 13.7 CH₃), 19.9 CH_3), 14.0 (Bu [SnCH₂, (Bu ${}^{1}J({}^{119,117}SnC) = 322$ unresolved], 26.3 (CH₂), 28.5 (CH₂), 28.9 (CH₂), 34.2 (SnCH₂), 42.3 (NCH₃), 56.9 (NCH₂), 200.4 (CN); ¹¹⁹Sn NMR: 21.0; Mössbauer: IS 1.39, QS 2.19, Γ 0.96.

2.3.2. $[{}^{n}Bu_{2}Sn(S_{2}CN(CH_{3})C_{4}H_{9})_{2}]$ (5)

Orange oil, 66% yield, microanalysis (required for $C_{20}H_{42}N_2S_4Sn$); C, 43.1 (43.1); H, 7.6 (7.6); N, 5.0 (5.0); ¹H NMR: 0.87 (6H, t, J = 7.2, Bu CH₃), 0.89 (6H, t, J = 7.2, Bu CH₃), 1.32 (4H, m, CH₂), 1.35 (4H, m, CH₂), 1.63 (4H, m, J = 7.5, CH₂), 1.84 (4H, m, CH₂), 1.95 (4H, m, CH₂), 3.32 (6H, s, NCH₃), 3.78 (4H, t, J = 7.7, NCH₂); ¹³C NMR: 13.4 (Bu CH₃), 13.5 (Bu CH₃), 17.4 [SnCH₂, ¹J(^{119,117}SnC) = 334 unresolved], 19.7 (CH₂), 26.8 (CH₂), 28.6 (CH₂), 28.9 (CH₂), 42.7 (NCH₃), 57.1 (NCH₂), 198.2 (CN); ¹¹⁹Sn NMR: – 341.3; Mössbauer: IS 1.52, QS 2.89, Γ 0.92.

2.3.3. $[MeSn(S_2CN(CH_3)C_4H_9)_3]$ (7)

Yellow solid, 62% yield, m.p. 72–73 °C, microanalysis (required for $C_{19}H_{39}N_3S_6Sn$); C, 36.5 (36.8); H, 6.5 (6.3); N, 6.5 (6.8); ¹H NMR: 0.88 (9H, t, J = 7.0, Bu CH_3), 1.28 (6H, m, J = 7.8, CH_2), 1.64 (6H, m, J = 7.4, CH_2), 1.85 [3H, s, ²J(^{119,117}SnH) = 59.3, 57.4, SnC H_3], 3.29 (9H, s, NC H_3), 3.69 (6H, t, J = 7.4, NC H_2); ¹³C NMR: 14.1 [SnC H_3], 14.3 (Bu CH_3), 20.4 (CH_2), 29.3 (CH_2), 43.5 (NC H_3), 58.4 (NC H_2), 201.1 (CN); ¹¹⁹Sn NMR: -605.2 (53%), -780.5 (100%); Mössbauer IS 1.13, QS 1.92, Γ 1.18.

2.3.4. $[^{n}BuS([S_{2}CN(CH_{3})C_{4}H_{9})_{3}]$ (8)

White solid, 51% yield, microanalysis (required for $C_{22}H_{45}N_3S_6Sn$); C, 39.3 (39.9); H, 6.7 (6.9); N, 6.2 (6.3); ¹H NMR: 0.79 (9H, t, J = 7.1, Bu CH₃), 1.01 (3H, t, J = 7.3, Bu CH₃), 1.10 (6H, m, J = 7.7, CH₂), 1.40 (6H, m, J = 7.3, CH₂), 1.58 (2H, m, J = 7.3, CH₂), 1.87 (2H, m, CH₂), 2.49 (2H, m, SnCH₂), 2.92 (9H, s, NCH₃), 3.44 (6H, t, J = 7.7, NCH₂); ¹³C NMR: 14.2 (Bu CH₃), 14.5 (Bu CH₃), 20.4 [SnCH₂], 26.1 (CH₂), 29.4 (CH₂), 30.4 (CH₂), 34.7 (CH₂), 42.9 (NCH₃), 58.2 (NCH₂), 192.8 (CN); ¹¹⁹Sn NMR: -580.2 (48%), -807.0 (100%); Mössbauer: IS 1.25, QS 1.84, Γ 1.04.

2.3.5. $[PhSn(S_2CN(CH_3)C_4H_9)_3]$ (9)

Pale yellow solid, 76% yield, m.p. 128–130 °C, microanalysis (required for $C_{24}H_{41}N_3S_6Sn$); C, 42.1 (42.2); H, 6.0 (6.1); N, 6.2 (6.2); ¹H NMR: 0.94 (9H, t, J = 6.2,

Bu CH₃), 1.35 (6H, m, J = 7.3, CH₂), 1.71 (6H, m, J = 5.5, CH₂), 3.34 (9H, s, NCH₃), 3.71 (6H, t, J = 7.1, NCH₂), 7.36 (3H, m, ArH), 7.97 [2H, d, ${}^{3}J = 7.9$, ${}^{2}J({}^{119}SnH) = 37.7$, ArH); ${}^{13}C$ NMR: 13.8 (Bu CH₃), 19.9 (Bu CH₂), 28.9 (Bu CH₂), 43.2 (NCH₃), 58.3 (NCH₂), 128.9 (ArC), 130.7 (ArC), 131.5 (ArC), 150.8 (ArC), 191.7 (CN); ${}^{119}Sn$ NMR: -654.6 (100%), -834.1 (45%); Mössbauer: IS 1.11, QS 1.81, Γ 0.82.

2.4. X-ray crystallography

A crystal of **3** of approximate dimensions $0.25 \times 0.25 \times 0.20$ mm was used for data collection. Crystal data: $C_{24}H_{27}NS_2Sn$, M = 512.28, triclinic, a = 9.837(2), b = 9.896(2), c = 14.140(3) Å, $\alpha = 72.73(2)$, $\beta = 72.04(2)$, $\gamma = 68.81(2)^\circ$, U = 1193.9(4) Å³, space group $P\overline{1}$ (No.2), Z = 2, $D_{calc} = 1.425$ g cm⁻³, μ (Mo K α) = 1.254 mm⁻¹, F(000) = 520. Crystallographic measurements were made at 293(2) K on a CAD4 automatic four-circle diffractometer in the range $2.26 < \theta < 24.97^\circ$. Data (4583 reflections) were corrected for Lorentz and polarization but not for absorption. In the final least-squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant.

The solution of the structure (SHELX86) [34] and refinement (SHELX93) [35] converged to a conventional [i.e. based on 3576 F^2 data with $F_o > 4\sigma(F_o)$] $R_1 = 0.0206$ and $wR_2 = 0.0531$. Goodness-of-fit = 0.965. The maximum and minimum residual densities were 0.319

and -0.271 e Å⁻³, respectively. The asymmetric unit, shown in Fig. 1 along with the labelling scheme used selected metrical data, and was produced using ORTEX [36].

Crystals of [PhSn(S₂CN(CH₃)C₄H₉)₃] (9) were also grown and belong to the triclinic crystal class (a =9.202, b = 10.901, c = 17.039 Å; $\alpha = 103.055$, $\beta = 93.97$, $\gamma = 108.151^{\circ}$). Although the heavy atom framework of the molecule was evident, no complete molecular model was refineable in either triclinic space group suggesting some subtle form of crystal twinning.

2.5. Chemical vapour deposition studies

Nitrogen (99.99%) and H₂S (99.9%) were obtained by BOC and used as supplied. Coatings were obtained on glass coated with a SiCO barrier layer that inhibited diffusion of ions from the glass. Atmospheric pressure CVD experiments were conducted on $225 \times 89 \times 4$ mm pieces using a horizontal bed cold wall APCVD reactor. The glass was cleaned by washing with petroleum ether (60-80) and isopropanol and air-dried prior to use. The glass was heated by a flat-bed graphite block that contained three Whatman cartridge heaters. The temperature of the graphite block was monitored by a Pt-Rh thermocouple. Thermocouple measurements indicated that temperature gradients of less than 5 °C at 500 °C were noted across glass substrates. All gas handling lines, regulators and flow valves were made of stainless steel and were 1/4" internal diameter except



Fig. 1. The asymmetric unit of **3** showing the labelling scheme used in the text and tables. Thermal ellipsoids are at the 30% probability level. Selected metrical data: Sn(1)-C(1) 2.152(2), Sn(1)-C(7) 2.130(2), Sn(1)-C(13) 2.148(2), Sn(1)-S(1) 2.4631(9), Sn(1)-S(2) 3.084(1), S(1)-C(19) 1.753(3), S(2)-C(19) 1.668(3) Å; C(7)-Sn(1)-C(1) 108.42(9), C(13)-Sn(1)-C(1) 105.28(9), C(7)-Sn(1)-C(13) 114.50(9), C(1)-Sn(1)-S(1) 89.47(6), C(7)-Sn(1)-S(1) 115.31(6), C(13)-Sn(1)-S(1) 119.42(6), $C(1)-Sn(1)-S(2) 152.13(7)^\circ$.

for the inlet to the mixing chamber and the exhaust line from the apparatus, which were 1/2" i.d. In these experiments three gas lines were used; two for nitrogen and one for a nitrogen/hydrogen sulfide line. The gases came directly from cylinders. Gas flows were adjusted using suitable regulators (spectrol 50S for the H₂S line) and flow controllers. The exhaust from the reactor was vented directly into the extraction system of a fume cupboard. All of the apparatus was baked out with plain nitrogen at 150 °C for 3 h before and after the runs. Deposition experiments were conducted by heating the horizontal bed reactor to the required temperatures before diverting one of the nitrogen lines through the bubbler and hence to the reactor. Bubbler temperatures were set at 82-88 °C for [SnMe₃(S₂CNMeBu)] and 110-135 °C for [SnBu(S₂CNMeBu)₃]. Deposition experiments were timed by stop-watch and were typically for 3 min. The precursors were mixed with a nitrogen diluted H₂S flow 1 cm before the mixing chamber of the coater (a full description of the APCVD apparatus used can be found in a previous paper [24]). At the end of the deposition the bubbler line was closed and only plain nitrogen passed over the substrate. The glass substrate was allowed to cool with the graphite block to approximately 60 °C before it was removed. Coated substrates were handled and stored in air. The large coated glass sample was broken up into approximately 1×1 cm squares for subsequent analysis by EDAX, SEM and UV studies. Large pieces of glass (ca. 4×4 cm) were used for sheet resistance, X-ray powder diffraction, Raman and Scotch tape tests.

X-ray powder diffraction patterns were measured on a Philips X-pert diffractometer using unfiltered Cu K α ($\lambda_1 = 1.5045$ Å, $\lambda_2 = 1.5443$ Å) radiation in the reflection mode using glancing incident angle. UV–Vis spectra were recorded in the range 200–1000 nm using a Shimadzu double beam instrument, band gaps were calculated by the direct method. SEM/EDAX was obtained on a Hitachi S570 instrument using the KEVEX system. Raman spectra were acquired on a Renishaw Raman System 1000 using a helium–neon laser of wavelength 632.8 nm. The Raman system was calibrated against the emission lines of neon. Reflectance/ transmission optical spectra were determined on a Xeiss miniature spectrometer.

3. Results

3.1. Synthesis of tin dithiocarbamates

Mono-, di- and tri-organotin derivatives of the unsymmetrical dithiocarbamic acid $CH_3(C_4H_9)NCS_2H$ were prepared by reaction of its lithium salt with the appropriate organotin chloride (Eq. (1)).

Compounds 3, 4, 6-9 are low melting point solids (80-125 °C) while compounds 1, 2 and 5 are oils. Yields were in the range 51–94% and generally decrease as the degree of substitution increases. All species are air-stable and soluble in common organic solvents. All of 1-9 had satisfactory microanalytical data and the expected ¹H and ¹³C NMR spectra; typical ^{1,2}J couplings were observed, for example 1 showed ${}^{1}J({}^{119,117}SnC) = 382$, 366 Hz and ${}^{2}J({}^{119,117}SnH) = 57.2$, 52.0 Hz. Mössbauer data for the series of monoorganotin compounds (7-9) (quadrupole splittings (qs): 1.81-1.92 mm s⁻¹) are uninformative as the regions associated with coordination number = 4(1.3-2.1 mm) s^{-1}), 5 (1.6–2.4 mm s^{-1}) and 6 (1.6–2.4 mm s^{-1}) are all very similar. Data for the triorganotin compounds 1-3 (qs: 1.79-2.19 mm s⁻¹) are consistent with essentially tetrahedral coordination about the metal (1.5-2.8)mm s⁻¹) while quadrupole splitting data for the diorganotin species $(2.31-2.89 \text{ mm s}^{-1})$ reflect weakly chelating dithiocarbamate groups [37]. ¹¹⁹Sn NMR chemical shifts are more sensitive to coordination number than Mössbauer quadrupole splitting values, and for each of the three series $(n = 3, \delta = 21, 22, -190;$ $n = 2, \ \delta = -341, \ -349, \ -505; \ n = 1, \ \delta = -780,$ -580, -834 ppm, for R = Me, Bu, Ph, respectively) the shifts are upfield of purely tetrahedral analogues, e.g. $R_n Sn(SR)_{4-n}$ [38]. Collectively these data are consistent with some degree of chelation, albeit rather weak, by the dithiocarbamate towards the metal. This is consistent with the structure of 3 described below.

3.2. Crystal structure of $Ph_3Sn[S_2CN(CH_3)C_4H_9]$ (3)

The structure of **3** is shown in Fig. 1. While numerous tin-dithiocarbamate complexes are known [39], this is the first structurally-characterised example of which we are aware in which the ligand is unsymmetrically substituted. The coordination about tin in 3 is mid-way between tetrahedral and trigonal bipyramidal due to a weakly chelating dithiocarbamate group. Sn(1)-S(2) is significantly longer [3.084(1) Å] than Sn(1)-S(1) [2.4631(9) Å] and the nominally axial substituents are far from linearly arranged [S(2)-Sn(1)-C(1) 152.13(7)°]. The remaining groups bonded to tin do, however, expand the angles subtend

at the metal towards the 120° expected of equatorial substituents [114.50(9), 115.31(6), 119.42(6)°].

Crystallographic studies of organotin compounds containing one or more dithiocarbamates show that these ligands are rarely symmetrically bound to the tin, i.e. one Sn–S bond is longer than the other [39–44]. The structure of **3** is directly comparable with that of [Ph₃Sn(S₂CNEt₂)] where the chelating C=S \rightarrow Sn bond is 3.11 Å [45]. Hall and Tiekink have shown how the electron donating/withdrawing effect of the other ligands bound to tin markedly affect both the anisobidentate nature of the Sn–S chelation (Δ Sn–S) and the solid state structure for compounds of the type R₂Sn(S₂CNR'₂)₂ (R = alkyl, aryl, vinyl, chloride; R' = alkyl) [39]. We have recently reported the structures of [BuSn(dtc)₂Cl] and [BuSn(dtc)Cl₂] (dtc = S₂CNEt₂) [46].

While crystals of the monoorganotin (9) were also obtained, it proved impossible to locate and refine adequately a complete molecular entity. The heavy atom (Sn, S) framework was, however, clearly evident and suggested a seven-coordinate pentagonal bipyramidal geometry about tin.

3.3. Chemical vapour deposition

APCVD using the two unsymmetrical dithiocarbamate precursors [SnMe₃(S₂CNMeBu)] (1) and [SnBu(S₂CNMeBu)₃] (8) has been studied. In the absence of H₂S no coating could be grown from either precursor. The unsymmetrical dithiocarbamates were, however, sufficiently volatile to give good carry over of the precursor with bubbler temperatures set at 85 °C for 1 and 110 °C for 8. In the presence of a minimal flow of H₂S (less than 1% of the gas stream), both precursors produced grey tin(II) sulfide films at substrate temperatures in excess of 500 °C. From 1 no coating could be grown at a substrate temperature of less than 350 °C. At 450 °C the coatings from 1 were brown and consisted of Sn_2S_3 with a trace of SnS_2 . In all of the depositions the coatings were only on the leading edge of the glass and covered the first 4 cm of the plate. Growth rates were at best approximately 150 nm min⁻¹. This compares with growth rates of 1000 nm min⁻¹ from equivalent reactions of SnCl₄ and H₂S.

3.4. Film characterisation

All the films formed from the APCVD of **1** or **8** with minimal H_2S flow passed the Scotch tape test. They could however be readily abraded with a scalpel. The film colours of grey for SnS and brown for Sn_2S_3 match previous deposition studies [24–26]. Raman spectra were very diagnostic showing bands at 307, 251, 234, 183 and 87 cm⁻¹ for the Sn_2S_3 film and bands at 288, 220, 189, 163 and 96 cm⁻¹ for the SnS films. The bands exactly matched data for bulk Sn_2S_3 and SnS and

previous thin film measurements [24-26]. The Sn₂S₃ film was predominantly brown in colour, however the edges of the film were yellow and Raman microscopy measurements indicated that SnS₂ was present. SEM measurements showed that the SnS films had a wavy agglomerated structure and the Sn₂S₃ material was composed of interlocked needles and as such matched those observed in previous APCVD experiments [24-26]. Films were of the order of 300 nm thick. EDAX analysis of all the films showed the presence of tin and sulfur. Direct quantification was difficult as the films were thin and the excitation voltage used produced significant breakthrough to the underlying glass. The films were too thin for quantification by X-ray diffraction. Band gap measurements gave a direct band gap of 1.20-1.25 eV for the SnS films.

4. Discussion

Tin unsymmetric dithiocarbamate complexes can be readily made by metathetical exchange of a lithium salt of a dithiocarbamic acid with an alkyltin chloride. The complexes were low melting point solids or oils that had sufficient vapour pressure to be used in APCVD experiments. X-ray crystallographic studies of **3** showed that the dithiocarbamate ligand was strongly bound through one sulfur atom to the tin, with the second sulfur atom only weakly bound. Hence the dithiocarbamate group was only weakly chelating. Tin NMR and Mössbauer measurements were in agreement with each dithiocarbamate ligand acting as essentially a unidentate ligand with only a weakly chelating second sulfur.

APCVD experiments of 1 and 8 show that these materials do not function as single-source precursors to tin sulfide thin films. At temperatures up to 550 °C in the absence of H₂S, no coating could be obtained on glass substrates. In the presence of a minimal flow of H₂S, SnS and Sn₂S₃ coatings could be grown. The absence of a film without a secondary sulfur source is a common feature of many APCVD systems we have investigated [24-26,28,29]. In the case of homoleptic tin thiolates this has been attributed to a facile disulfide elimination mechanism, that generates tin-metal which in turn can only form tin-sulfide in the presence of a secondary sulfur source such as H₂S. It was hoped that the use of chelating ligands such as dithiocarbamates would discourage a bis-ligand elimination pathway. However, the unsymmetric dithiocarbamates derivatives are essentially monodentate ligands with a weak secondary interaction rather than strongly chelating ligands, which may account for the lack of a film in the absence of H₂S. The formation of SnS films in the majority of the CVD experiments in the presence of H₂S is analogous to previous work, indicative of a

reduction of the metal centre [28,29]. It is also likely that the sulfur in the growing films comes form the H_2S and not the dithiocarbamate precursor.

5. Supplementary material

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 163857. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam. ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Dr D. Sheel and Dr K. Sandersen of Pilkington Glass PLC are thanked for useful discussion and for providing the reactor coater and undercoated glass for deposition experiments. Mr D. Knapp and Mr D. Morphett are thanked for help with construction of the APCVD rig. The EPSRC are acknowledged for grants GR/L54721 to K.C.M. and GR/L56442 and GR/ M82592 to I.P.P. Professor R.J.H. Clark is thanked for help in acquiring the Raman spectra.

References

- [1] T. Jiang, G.A. Ozin, J. Mater. Chem. 8 (1998) 1099.
- [2] R. Hertzenberg, Rev. Minerals 4 (1932) 33.
- [3] B. Polosz, W. Steurer, H. Schultz, Acta Crystallogr., Sect. B 46 (1990) 449.
- [4] M. Hell, Ger. Offen. DE 4,340,017 (Cl.C08J5/14), 1 June, 1995.
- [5] M. Geringer, PCT Int. Appl. WO 96 36,681 (Cl.C/O M 103/06), 21 November, 1996.
- [6] H.P. Rimmington, A.A. Balchin, J. Cryst. Growth 15 (1972) 51.
- [7] I. Oftedal, Z. Phys. Chem. 134 (1928) 301.
- [8] R. Kneip, D. Mootz, U. Severin, H. Wunderlich, Acta Crystallogr., Sect. B 38 (1982) 2022.
- [9] P. Boudjouk, D.J. Seidler, S.R. Bahr, G.J. McCarthey, Chem. Mater. 6 (1994) 2108.
- [10] M.B. Robin, P. Day, Adv. Inorg. Chem. Radiochem. 10 (1967) 247.
- [11] K. Deraman, S. Sakrani, B. Bismail, Y. Wahab, R.D. Gould, Int. J. Electronics 76 (1994) 917.
- [12] G.B. Dubrovski, N.S. Zhdanovich, Fiz. Tverd. Tela (Leningrad) 38 (1996) 272.
- [13] J.P. Singh, R.K. Bedi, Thin Solid Films 199 (1991) 9.
- [14] A. Ortiz, J.C. Alonso, M. Garcia, J. Toriz, J. Semicond. Sci. Technol. 11 (1996) 243.

- [15] R.D. Engleken, H.E. McCloud, C. Lee, M. Slayton, H. Goreishi, J. Electrochem. Soc. 134 (1987) 2696.
- [16] C.D. Lokhande, Mater. Chem. Phys. 28 (1991) 145.
- [17] P. Pramanik, P.K. Basu, S. Biswas, Thin Solid Films 150 (1987) 269.
- [18] M. Ristov, G. Sinadinovski, I. Grozdanov, M. Mitreski, Thin Solid Films 173 (1989) 53.
- [19] A.J. Varkey, Int. J. Mater. Prod. Technol. 12 (1997) 490.
- [20] V.V. Bhad, C.D. Iokhande, Bull. Electrochem. 7 (1991) 571.
- [21] M.T.S. Nair, P.K. Nair, J. Semicond. Sci. Technol. 6 (1991) 132.
- [22] A. Ortiz, S. Lopez, J. Semicond. Sci. Technol. 9 (1994) 2130.
- [23] H.M. Manasevit, W.I. Simpson, J. Electrochem. Soc. 122 (1975) 444.
- [24] L.S. Price, I.P. Parkin, T.G. Hibbert, K.C. Molloy, Adv. Mater. 4 (1998) 222.
- [25] L.S. Price, I.P. Parkin, A.M.E. Hardy, R.J.H. Clark, T.G. Hibbert, K.C. Molloy, Chem. Mater. 11 (1999) 1792.
- [26] I.P. Parkin, L.S. Price, A.M.E. Hardy, R.J.H. Clark, T.G. Hibbert, K.C. Molloy, J. Phys. IV France 9 (1999) Pr8.
- [27] L.S. Price, I.P. Parkin, M.N. Field, A.M.E. Hardy, R.J.H. Clark, T.G. Hibbert, K.C. Molloy, J. Mater. Chem. 10 (2000) 527.
- [28] G. Barone, T.G. Hibbert, M.F. Mahon, K.C. Molloy, L.S. Price, I.P. Parkin, A.M.E. Hardy, M.N. Field, J. Mater. Chem. 11 (2000) 464.
- [29] T.G. Hibbert, M.F. Mahon, K.C. Molloy, I.P. Parkin, L.S. Price, J. Mater. Chem. 11 (2001) 469.
- [30] T.G. Hibbert, M.F. Mahon, K.C. Molloy, I.P. Parkin, L.S. Price, I. Silaghi-Dumitrescu, 2001, submitted for publication.
- [31] M.R. Lazell, P. O'Brien, D.J. Otway, J.H. Park, Chem. Mater. 11 (1999) 3430.
- [32] P. O'Brien, D.J. Otway, J.R. Walsh, Thin Solid Films 315 (1998) 57.
- [33] K.C. Molloy, T.G. Purcell, K. Quill, I. Nowell, J. Organomet. Chem. 267 (1984) 237.
- [34] G.M. Sheldrick, SHELX 86S, A Computer Program for Crystal Structure Determination, University of Göttingen, Göttingen, Germany, 1986.
- [35] G.M. Sheldrick, SHELX 93, A Computer Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1993.
- [36] P. McArdle, J. Appl. Cryst. 28 (1995) 65.
- [37] A.G. Davies, P.J. Smith, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 2, Pergamon Press, Oxford, 1982, p. 519.
- [38] B. Wrackmeyer, Annu. Rep. NMR Spectrosc. 16 (1985) 73.
- [39] V.J. Hall, E.R.T. Tiekink, Main Group Met. Chem. 21 (1998) 245.
- [40] V.J. Hall, E.R.T. Tiekink, Main Group Met. Chem. 18 (1995) 611.
- [41] J.M. Hook, B.M. Linahan, R.L. Taylor, E.R.T. Tiekink, L. van Gorkom, L.K. Webster, Main Group Met. Chem. 17 (1994) 293.
- [42] D. Dakternieks, H. Zhu, D. Masi, C. Mealli, Inorg. Chem. 31 (1992) 3601.
- [43] K. Kim, J.A. Ibers, O.-S. Jung, Y.S. Sohn, Acta Crystallogr., Sect. C C43 (1987) 2317.
- [44] E. Kellö, V. Vrabel, I. Skacani, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. 51 (1995) 408.
- [45] P.F. Lindley, P. Carr, J. Cryst. Molec. Struct. 4 (1974) 173.
- [46] T.G. Hibbert, M.F. Mahon, K.C. Molloy, Main Group Met. Chem. 22 (1999) 235.