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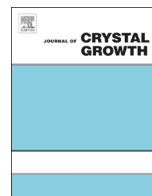




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Thin films of tin(II) sulphide (SnS) by aerosol-assisted chemical vapour deposition (AACVD) using tin(II) dithiocarbamates as single-source precursors



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ABSTRACT

The synthesis of the asymmetric dithiocarbamates of tin(II) with the formula $[\text{Sn}(\text{S}_2\text{CNRR}')_2]$ (where $\text{R}=\text{Et}$, $\text{R}'=n\text{-Bu}$ (**1**); $\text{R}=\text{Me}$, $\text{R}'=n\text{-Bu}$ (**2**); $\text{R}=\text{R}'=\text{Et}$ (**3**)) and their use for the deposition of SnS thin films by aerosol-assisted chemical vapour deposition (AACVD) is described. The effects of temperature and the concentration of the precursors on deposition were investigated. The stoichiometry of SnS was best at higher concentrations of precursors (250 mM) and at 450 °C. The direct electronic band gap of the SnS produced by this method was estimated from optical absorbance measurements as 1.2 eV. The composition of films was confirmed by powder X-ray diffraction (p-XRD) and energy dispersive analysis of X-rays (EDAX) spectroscopy.

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1. Introduction

Tin monosulphide (SnS) [1] is a promising candidate amongst the IV–VI semiconductors for sustainable photovoltaic and optoelectronic applications [2]. SnS has intense absorbance ($\alpha \sim 10^4 \text{ cm}^{-1}$) across the electromagnetic (EM) spectrum, and a direct band gap of 1.4 eV [3], similar to that of silicon, and can harvest solar radiation from the near-infrared region of the EM spectrum and upwards in energy. The constituent elements, tin and sulphur, are abundant, inexpensive, less toxic and generally less environmentally harmful as compared with materials such as lead sulphide (PbS) and cadmium sulphide (CdS). The SnS binary system is simpler compared to multicomponent materials with potential for photovoltaic applications such as copper zinc tin sulfides (CZTS) [4,5] and the copper indium gallium sulphides and selenides (CIGS, CIGSe) [6]. Theoretical solar conversion efficiency values of SnS are ca. 24% [7]. So far, solar cells using SnS absorbers with efficiencies of only ca. 2% have been developed [8], and thus the potential for improvement is great.

Processes used for deposition of SnS thin films include chemical bath deposition (CBD) [9], successive ionic layer adsorption and

reaction (SILAR) [10,11] and electrochemical deposition [12–14]. Other methods such as thermal evaporation [15], chemical vapour transport (CVT) [16], atomic layer deposition (ALD) [17,18], spray pyrolysis [19,20], dip deposition [21], and pyrolysis [22] have also been reported.

Chemical vapour deposition (CVD) using single-source precursors is a facile route to SnS thin films. Variations of CVD processes such as aerosol-assisted chemical vapour deposition (AACVD) [23,24] and atmospheric pressure chemical vapour deposition (APCVD) [25,26] have attracted attention for the deposition of SnS due to their ease of use and potential for scale up. AACVD in particular offers the advantage that less-volatile precursors can be used, thus widening the types of molecules that can be used to deposit thin films. Single-source precursors in particular offer an advantageous route in CVD especially, as complicating factors such as pre-reaction in the vapour can be avoided [27]. SnS thin films have been deposited by CVD from thiocarbamate precursors such as $\text{Sn}(\text{S}_2\text{CNET}_2)_4$ [28,29]. $\text{Sn}(\text{S}_2\text{CNET}_2)_4$, tin thiolates and dithiolates [25,28,30], as well as from tribenzyl tin(IV) chloridothiosemicarbazone compounds [23]. We have previously reported the deposition of SnS thin films by AACVD using heteroleptic di-organo tin(IV) bis-dialkyldithiocarbamate complexes of formula $[\text{Sn}(\text{C}_4\text{H}_9)_2(\text{S}_2\text{CN}(\text{RR}')_2)_2]$ (R , $\text{R}'=\text{ethyl}$; $\text{R}=\text{methyl}$, $\text{R}'=\text{butyl}$; R , $\text{R}'=\text{butyl}$; $\text{R}=\text{methyl}$, $\text{R}'=\text{hexyl}$) and $[\text{Sn}(\text{C}_6\text{H}_5)_2(\text{S}_2\text{CN}(\text{RR}')_2)_2]$ (R , $\text{R}'=\text{Et}$; $\text{R}=\text{Me}$, $\text{R}'=n\text{-Bu}$; R , $\text{R}'=n\text{-Bu}$; $\text{R}=\text{R}'=\text{Et}$) [31]. We report

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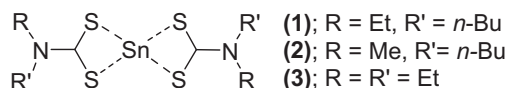


Fig. 1. The bis-(dialkylthiocarbamato)tin(II) complexes studied as precursors for producing SnS thin films by AACVD.

here the growth of SnS thin films using tin(II) complexes of general formula $[\text{Sn}(\text{S}_2\text{CNR}'')_2]$ (Fig. 1). These pre-cursors contain tin in the correct oxidation state for SnS, and may thus give a straightforward route towards this interesting material.

2. Experimental

2.1. General

Reagents and solvents were purchased from Sigma Aldrich or Fisher and used without further purification. All reactions were performed under inert atmosphere. The compounds produced were dried in vacuo at ambient temperature in a vacuum desiccator over calcium chloride.

2.2. Instrumentation

NMR spectra were recorded using a Bruker NMR instrument. Mass spectra were recorded using a Kratos Concept 1S instrument or a Micromass Platform II instrument. Melting points were recorded using a Stuart SMP-10. Microanalysis was performed using a Thermo Scientific Flash 2000 Organic Elemental Analyser by the University of Manchester analytical service. Thermogravimetric analyses were performed using MT TGA/DSC 1. FTIR spectra of compounds were measured using a Specac ATR. Single crystal X-ray diffraction was run using a Bruker Prospecor diffractometer and copper K_{α} radiation ($\lambda = 1.54178 \text{ \AA}$). The structure was solved by direct methods and refined by full-matrix least-squares fit on F^2 . All non-H atoms were refined anisotropically. All calculations were carried out using SHELXTL [32]. p-XRD patterns of thin films deposited on glass substrate were measured using a Bruker AXS D8 Discover diffractometer, using copper K_{α} radiation ($\lambda = 1.54178 \text{ \AA}$). Films were scanned repetitively over a range of diffraction angles (2θ) using a step size of 0.05° with a dwell time of 0.5 s. SEM analysis was performed using a Philips XL-30 scanning electron microscope in secondary electron mode, and EDAX carried out using a DX4 instrument. Films were coated with elemental carbon using an Edwards model E306A thermal evaporator prior to SEM and EDAX analyses. EDAX analysis using Espirit software included an automatic correction for carbon coating. Band gaps were measured using a Varian Cary 5000 UV–vis absorption spectrometer.

2.3. Synthesis of $[\text{Sn}(\text{S}_2\text{CN}((\text{C}_2\text{H}_5)(\text{C}_4\text{H}_9))_2)]$ (**1**)

N,N-ethylbutyl amine (5.0 g, 49 mmol, 1.0 eq.) and NaOH (2.0 g, 49.4 mmol) in methanol (100 mL) were mixed and cooled to $0-5^\circ\text{C}$, followed by the dropwise addition of carbon disulphide (3.8 g, 49 mmol, 1.0 eq.). The resulting mixture was then stirred for a further 30 min, followed by the dropwise addition of tin(II) chloride (4.7 g, 24.5 mmol, 0.5 eq.) in methanol (25 mL). The reaction mixture was stirred for a further hour, after which time a creamy or pale yellow powder formed which was filtered and washed with hexane and dried and kept under vacuum to give the title product as a cream powder. Yield = 3.1 g (27%). M.pt.: $121-125^\circ\text{C}$; Elemental analysis: Calc. for $\text{C}_{14}\text{H}_{24}\text{N}_2\text{S}_4\text{Sn}$: C 35.7 H 6.0 N 5.9 S 27.2 Sn 25.2%. Found C 35.8 H 5.8 S 26.8 Sn 24.4%. FTIR ($\nu_{\text{max}}/\text{cm}^{-1}$) 2953(w), 2926(w), 2865(w) 1489(s) 1441(m) 1299

(m), 1253(m), 1204(m), 1189(m) 1121(m). ^1H NMR (400 MHz, CDCl_3) δ ppm: 0.96 (6H, t, Bu CH_3), 1.38 (8H, q, CH_2), 1.77 (6H, t, CH_3), 3.72 (4H, q, Et NCH_2), 3.82 (4H, t, $J = 8 \text{ Hz}$, Bu NCH_2). ^{119}Sn NMR (149 MHz, CDCl_3) δ ppm: -522 (s). Crystals of (**1**) suitable for single crystal X-ray diffraction were grown from diffusion of hexane into a chloroform solution of the tin(II) complex.

2.4. Synthesis of $[\text{Sn}(\text{S}_2\text{CN}((\text{CH}_3)(\text{C}_4\text{H}_9))_2)]$ (**2**)

(**2**) was synthesised by the method presented for complex (**1**), but using *N,N*-methylbutyl amine (4.3 g, 49 mmol, 1.0 eq.) and tin(II) chloride (4.7 g, 24.5 mmol, 0.5 eq.) to give a pale yellow powder. Yield = 4.1 g (35%). Elemental analysis: Calc. for $\text{C}_{14}\text{H}_{24}\text{N}_2\text{S}_4\text{Sn}$: C 32.4 H 5.5 N 6.3 S 28.9 Sn 26.8%. Found C 32.2 H 5.4 N 6.1 S 23.0 Sn 25.6%. M.pt. $125-128^\circ\text{C}$. FTIR ($\nu_{\text{max}}/\text{cm}^{-1}$): 2924.9 (s), 2854(w), 1489 (s), 1385 (s), 1236 (m), 1188 (s), 1142 (m), 1075 (m) 966 (s). ^1H NMR (400 MHz, CDCl_3) δ ppm: 0.9 (6H, t, $J = 8 \text{ Hz}$, Bu CH_3), 1.3 (4H, q, Bu CH_2), 1.75 (4H, m, Bu CH_2) 3.18 (6H, s, $J = 8 \text{ Hz}$, NCH_3), 3.58 (4H, t, $J = 7.35 \text{ Hz}$, NCH_2). ^{119}Sn NMR (149 MHz, CDCl_3) δ ppm: -538 (s).

2.5. Synthesis of $[\text{Sn}(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)]$ (**3**)

(**3**) was synthesised by the addition of tin(II) chloride (4.1 g, 22 mmol, 1.0 eq.) in methanol (50 mL) to the trihydrated monosodium salt of diethyl dithiocarbamate (10 g, 44 mmol, 2.0 eq.) in methanol (100 mL). The product precipitated as a fine yellow powder which was isolated by filtration, washed with hexane ($2 \times 20 \text{ mL}$) and dried under vacuum to furnish the title product. Yield = 5.4 g (59%). M.pt. $120-128^\circ\text{C}$. Elemental analysis: Calc. for $\text{C}_{16}\text{H}_{32}\text{N}_2\text{S}_4\text{Sn}$: C 28.9 H 4.9 N 6.7 Sn 28.6%. Found C 28.3 H 4.8 N 6.5 Sn 27.0%. M.pt. $123-125^\circ\text{C}$. FTIR ($\nu_{\text{max}}/\text{cm}^{-1}$): 2965 (w), 2941 (w), 1509 (s), 1483 (s), 1350 (m), 1260 (m), 1142 (m), 1199 (m) 1131 (m). ^1H NMR (400 MHz, CDCl_3) δ ppm: 0.90 (6H, t, $J = 8 \text{ Hz}$, Hex CH_3), 1.35 (12H, t, Hex Et, CH_3), 3.08 (8H, q, $J = 16 \text{ Hz}$, NCH_2). ^{119}Sn NMR (149 MHz, CDCl_3) δ ppm: -523 (s).

2.6. Deposition of tin sulphide thin films by aerosol assisted chemical vapour deposition (AACVD) using tin(II) dithiocarbamate precursors.

In a typical deposition, 0.4–2.5 mmol of precursor (**1**), (**2**) or (**3**) was dissolved in 10 mL of THF in a two-necked round-bottom flask. The AACVD apparatus used for deposition has been described elsewhere [31]. Briefly, A quartz tube reactor containing borosilicate glass substrates ($\sim 1 \text{ cm} \times 2 \text{ cm}$ and 1 mm thick laid short end-to short end) were placed in a pre-warmed Carbolite furnace. The reactor tube was connected to the flask with a piece of reinforced rubber tubing. The precursor solution was then set up over an ultrasonic humidifier which formed the aerosol. The aerosol droplets were carried to the reactor tube by a constant flow of argon ($160-180 \text{ cm}^3 \text{ min}^{-1}$) into the round-bottom flask for thermal decomposition to deposit products onto the substrate.

3. Results and discussion

3.1. Synthesis of precursors

Tin(II) dithiocarbamates (**1**) and (**2**) were prepared in good yield from the reaction of carbon disulphide with a secondary amine in the presence of a base, followed by metathesis of tin(II) chloride to yield the homoleptic tin(II) complexes. Compound (**3**) was accessed directly from metathesis of SnCl_2 with the commercially available sodium salt of diethyl dithiocarbamate. ^{119}Sn NMR spectra of (**1**)–(**3**) showed single peaks in the range -520 to -540 ppm, indicative of a single tin(II) environment.

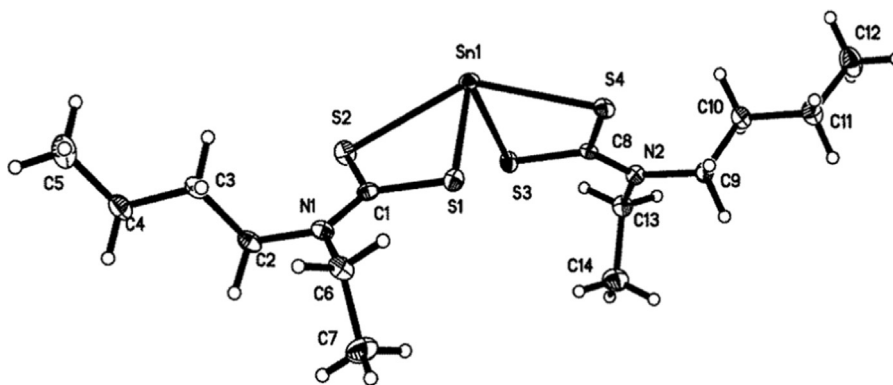


Fig. 2. Crystal structure of **(1)** from X-ray diffraction data. Selected bond lengths (Å) and bond angles ($^{\circ}$): Sn1–S1, 2.570(7); Sn1–S2, 2.835(8); Sn1–S4, 2.73(7); S(1)–Sn(1)–S(2), 66.40(2); S(3)–Sn(1)–S(4), 67.84(2); S(4)–Sn(1)–S(2), 140.36(2); S(1)–Sn(1)–S(3), 95.89(2); S(1)–Sn(1)–S(4), 85.65(2); S(3)–Sn(1)–S(2), 86.89(2).

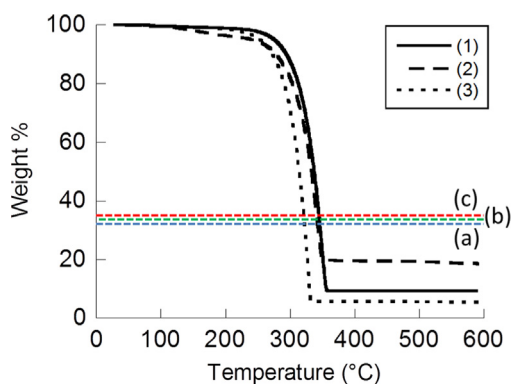


Fig. 3. TGA traces of compounds **(1)**–**(3)**. Horizontal lines (a), (b) and (c) represent the theoretical % weight loss required to produce SnS from compounds **(1)**, **(2)** and **(3)**: 32% (blue), 34% (green) and 36% (red) respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.2. Single crystal X-ray diffraction studies of a precursor.

Crystals of complex **(1)**, grown by diffusion of hexane into a chloroform solution of **(1)**, were studied by single crystal X-ray diffraction. The tin(II) ion is coordinated to four sulphur atoms via two bidentate dithiocarbamate ligands (Fig. 2). Each ligand forms a four-membered SnS_2C ring with a short (2.5650(7), 2.5762(7) Å) and a long (2.8356(8), 2.7379(7) Å) Sn–S distances. The sulphur atoms with long Sn–S bonds are pushed further apart (S(4)–Sn(1)–S(2) angle 140.36°) while those with short Sn–S bonds are closer together (S(3)–Sn(1)–S(1) angle is 95.89°). The coordination environment of the tin centre is best described as a distorted square pyramid with the formal lone pair of electrons on Sn(II) occupying the apex of the pyramid. Data for the crystal structure is given in the Supporting Information.

3.3. Thermogravimetric analysis.

The decomposition of the complexes was studied using thermogravimetric analysis (TGA) in the range 25–600 $^{\circ}\text{C}$ at a heating rate of $10^{\circ}\text{C min}^{-1}$ under a nitrogen atmosphere (Fig. 3). Complexes **(1)**–**(3)** showed a single-step decomposition, with the majority of the mass loss occurring in the temperature range 300–400 $^{\circ}\text{C}$. Solid residues which remain after for **(1)** and **(2)** are ca. 10% of the original weight for both complexes. Similarly, **(3)** decomposes in a single step to leave ca. 17% of residue. For precursors **(1)** and **(2)** the theoretical final mass should be 32% and 34% of the original mass for decomposition to SnS respectively, whilst for **(3)** this figure is 36%. More weight is lost

than the theoretical amount required for the production of SnS in all cases. The experimental weight losses do not equate to the oxides of tin (SnO or SnO_2) nor to elemental sulphur. We therefore presume that during the TGA analysis that some sublimation occurs in the major weight loss step before stable products are produced.

3.4. Deposition of thin films by AACVD.

Thin films of tin(II) sulphide were deposited on glass substrates by AACVD using THF solutions of precursors **(1)**, **(2)** and **(3)** at 4 mM concentration, using deposition temperatures of 450 $^{\circ}\text{C}$ and 500 $^{\circ}\text{C}$. Grey adherent films were observed in all cases. The deposited films were analysed by powder X-ray diffraction (p-XRD). The p-XRD patterns of thin films deposited from complexes **(1)**–**(3)** at 450 $^{\circ}\text{C}$ and 500 $^{\circ}\text{C}$ can be partly indexed to orthorhombic SnS (PDF Card No. 00-033-1375, herzenbergite) (Fig. 4), with the relatively highest intensity peak observed at $2\theta=31.50^{\circ}$, corresponding to the (111) plane. Peaks could be indexed as SnS: 25.98° (120), 27.44° (021), 30.44° (101), 39.01° (131), 45.48° (002), 48.51° (211) and 51.04° (122). Diffraction patterns show an additional peak at 33.50° which has been attributed to a SnO_2 cassiterite phase [31].

Scanning electron microscopy (SEM) was used to investigate the morphology of SnS thin films produced from AACVD. Bundles of sheets consisting of small crystallites were deposited with precursor **(1)**. Precursor **(2)** gave uniformly distributed cross linked bundles of sheets at 450 $^{\circ}\text{C}$ and 500 $^{\circ}\text{C}$. Bundles of sheets were also produced from precursor **(3)** at both temperatures (Fig. 5). A summary of the morphologies of films is presented in Table 1. Analysis of the SnS films by EDAX spectroscopy revealed that the Sn:S stoichiometry was quite variable (Table 1). Films produced at 450 $^{\circ}\text{C}$ and 500 $^{\circ}\text{C}$ from precursor **(1)** generally gave near-stoichiometric (percentage basis) SnS (55:45 and 49:51 respectively), whereas precursors **(2)** and **(3)** gave non-stoichiometric, tin-rich films in the ratio ca. 60:40, at both deposition temperatures.

3.5. Investigating the effect of precursor concentration

An investigation into the effect of the precursor concentration in the THF solution used for AACVD was conducted. Intensities of p-XRD diffraction peaks obtained from films deposited at 450 $^{\circ}\text{C}$ using four different concentrations of complexes **(1)**–**(3)** (80 mM, 170 mM and 250 mM) are shown in Fig. 6. The diffraction peaks from films deposited were again indexed to orthorhombic SnS (herzenbergite, PDF Card No. 00-033-1375). The intensity of the SnO_2 peak decreased with increasing concentrations of precursor. At a concentration of 250 mM the peak corresponding to SnO_2 was

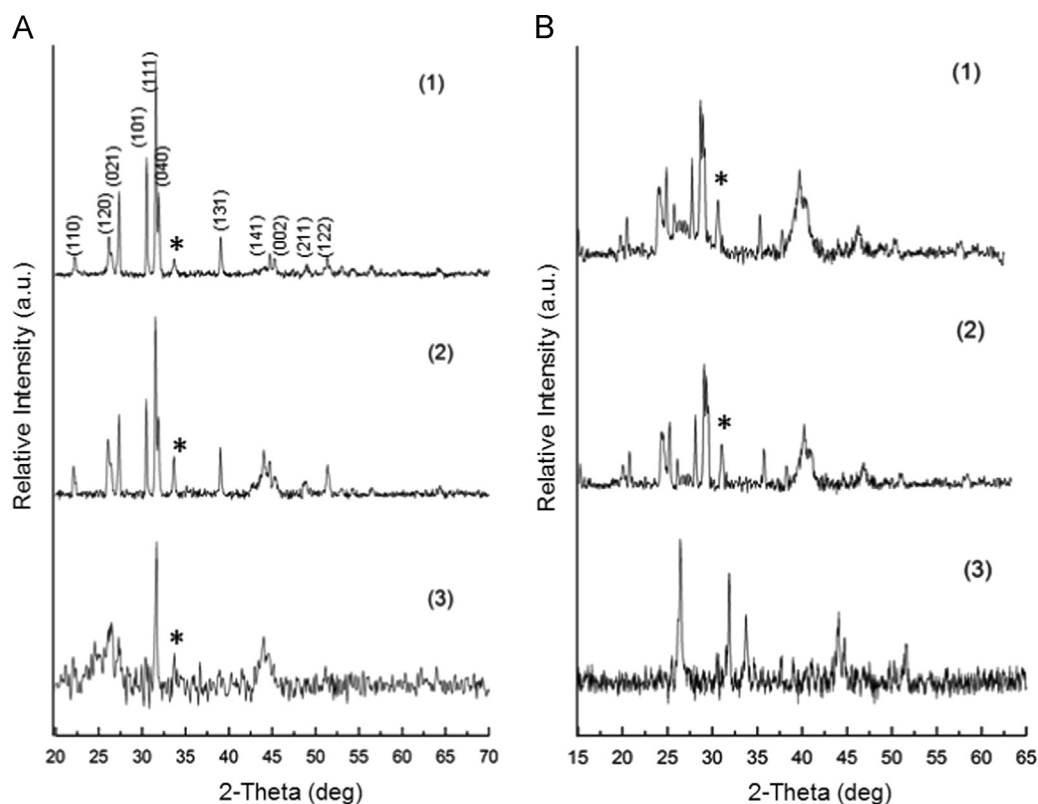


Fig. 4. p-XRD patterns of tin sulphide thin films deposited on glass substrates by AACVD using 40 mM of precursors (1)–(3) at A) 450 °C and B) 500 °C. Films were deposited over 45 min in all cases. The (*hkl*) reflections corresponding to crystallographic planes in SnS (herzenbergite, PDF Card No. 00-033-1375) are labelled for (1) at 450 °C only for clarity purposes. *=reflections attributed to SnO₂.

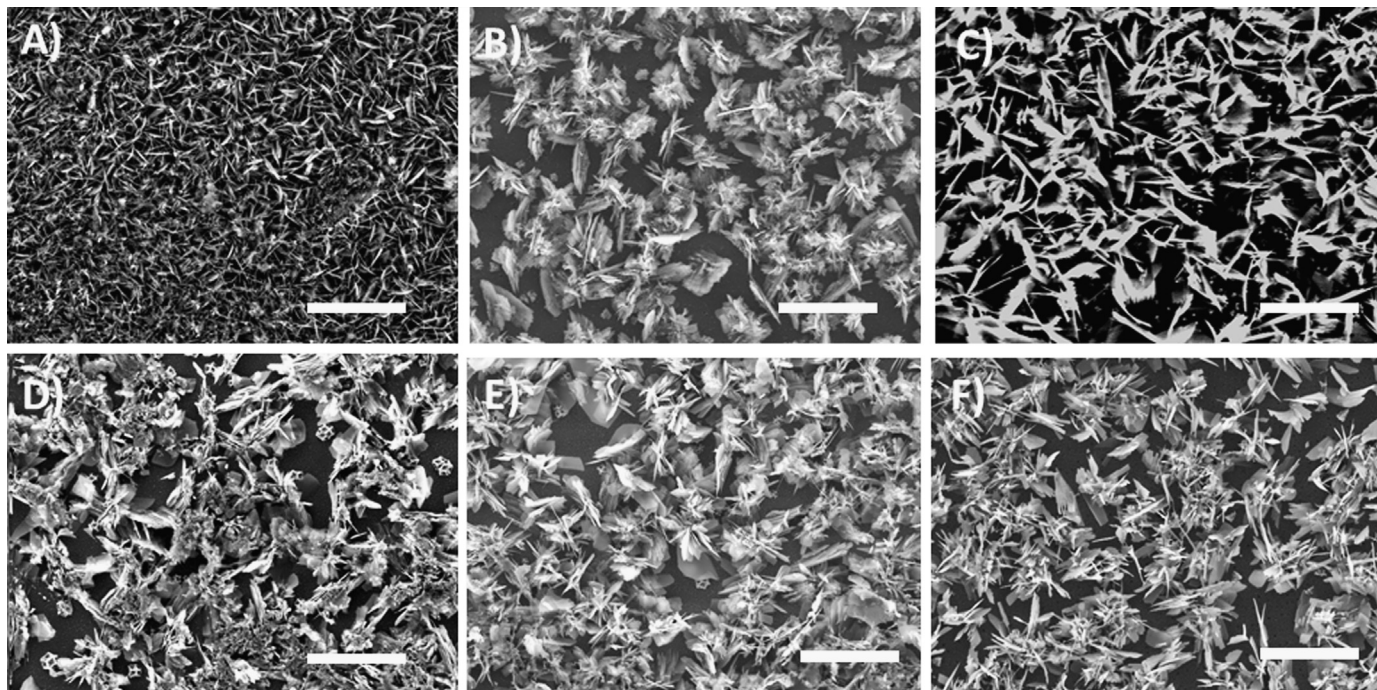


Fig. 5. Secondary electron SEM images of thin films deposited at different temperatures on glass substrates using precursors (1)–(3) at a concentration of 40 mM. (A) (1) at 450 °C, (B) (2) at 450 °C, (C) (3) at 450 °C. All films were deposited over 45 min. Scale bars 10 μm. (D) (1) at 500 °C, (E) (2) at 500 °C, (F) (3) at 500 °C. Scale bars 20 μm.

diminished to a vanishingly low intensity. Thus it was possible to produce pure films of SnS, eliminating contamination by oxides of tin.

Higher concentrations of precursors (1)–(3) at 450 °C led to films of a generally similar crystallite morphology by SEM (Fig. 7).

The morphologies of the films at every temperature and concentration investigated in this study are summarised in Table 1.

The elemental composition of thin films deposited from using higher concentrations of all precursors was investigated. EDAX spectroscopy revealed the tin: sulphur stoichiometry of films

(Table 1). At higher concentrations the Sn:S ratio approaches 1:1 for both precursors (2) and (3) at 450 °C. The same trend was also observed for SnS films deposited using (1) as the single-source precursor, but for this precursor the stoichiometry by EDAX spectroscopy was 1:1 using a 250 mM solution. In general then, the use of higher concentrations of precursors is crucial for the formation of stoichiometric or near-to-stoichiometric films of SnS for all precursors studied. The results are summarised in Fig. 8 and the EDAX data used to plot the graph is presented in Table 1.

3.6. Determination of band gap for a stoichiometric SnS film.

UV–vis absorption spectroscopy was used to estimate the optical band gap of the best film of SnS, grown using 250 mM precursor (1) and a deposition temperature of 450 °C.

Extrapolation of the linear region of the plot of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$), where α is the wavelength-dependant absorption coefficient of SnS (for these films, $\alpha(\lambda) > 10^4 \text{ cm}^{-1}$ in the linear region), estimates a direct band gap of 1.2 eV (Fig. 9). Measured direct band gaps of thin films of SnS have previously been quoted in the range 1.0–1.7 eV depending on the deposition method used. For instance, SnS films produced by Ray et al. using dip deposition with tin(II) chloride and thiourea precursors gave SnS with a direct band gap of 1.4 eV by photoconductivity measurements [21]. O'Brien and co-workers used optical spectroscopy to evaluate direct band gaps of SnS deposited from similar organo-tin(IV) dithiocarbamate complexes, with values for the films of SnS deposited from the equivalent precursor to (2) estimated as 1.2 eV, 1.2 eV, 1.6 eV and 1.7 eV for deposition temperatures of 400 °C, 450 °C, 500 °C and 530 °C respectively

Table 1

Summary of SnS films produced by AACVD: elemental composition from EDAX spectroscopy, morphology of films from SEM and optical band gaps obtained from precursors (1)–(3) at different temperatures and precursor concentrations.

Deposition temperature (°C)	Precursor concentration (mM)	EDAX (%)		Morphology	Band gap (eV)
		Sn	S		
[Sn(S₂CN(C₂H₄)(C₄H₉))₂] (1)					
450	40	55	45	Bundles of sheets	–
450	80	55	45	Bundles of sheets	–
450	170	51	49	Bundles of sheets	–
450	250	50	50	Bundles of sheets	1.2 eV, direct
500	40	49	51	Bundles of sheets	–
[Sn(S₂CN(CH₃)(C₄H₉))₂] (2)					
450	40	58	42	Bundles of sheets	–
450	80	58	42	Bundles of sheets	–
450	170	52	48	Bundles of sheets	–
450	250	53	47	Bundles of sheets	–
500	40	64	36	Bundles of sheets	–
[Sn(S₂CN(C₂H₄)₂)₂] (3)					
450	40	59	41	Bundles of sheets	–
450	80	58	42	Bundles of sheets	–
450	170	54	46	Bundles of sheets	–
450	250	53	47	Bundles of sheets	–
500	40	61	39	Bundles of sheets	–

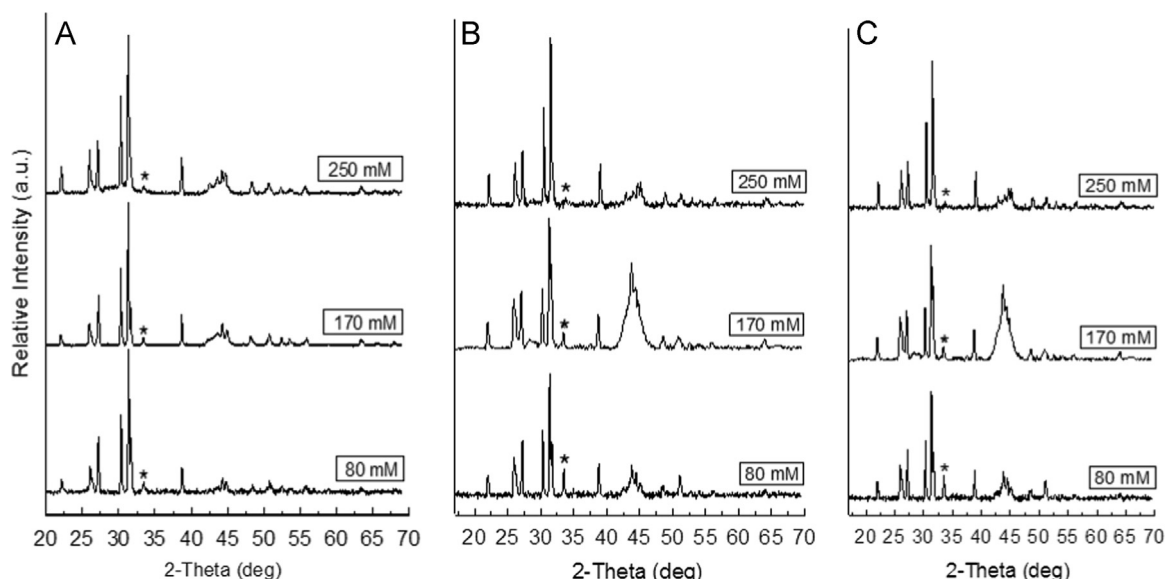


Fig. 6. p-XRD patterns of SnS thin films deposited on glass substrates by AACVD using (A) 80 mM, 170 mM and 250 mM of (1) at 450 °C, (B) 80 mM, 170 mM and 250 mM of (2) at 450 °C and (C) 80 mM, 170 mM and 250 mM of (3) at 450 °C. All films were deposited over 45 min. * = reflection attributed to SnO₂.

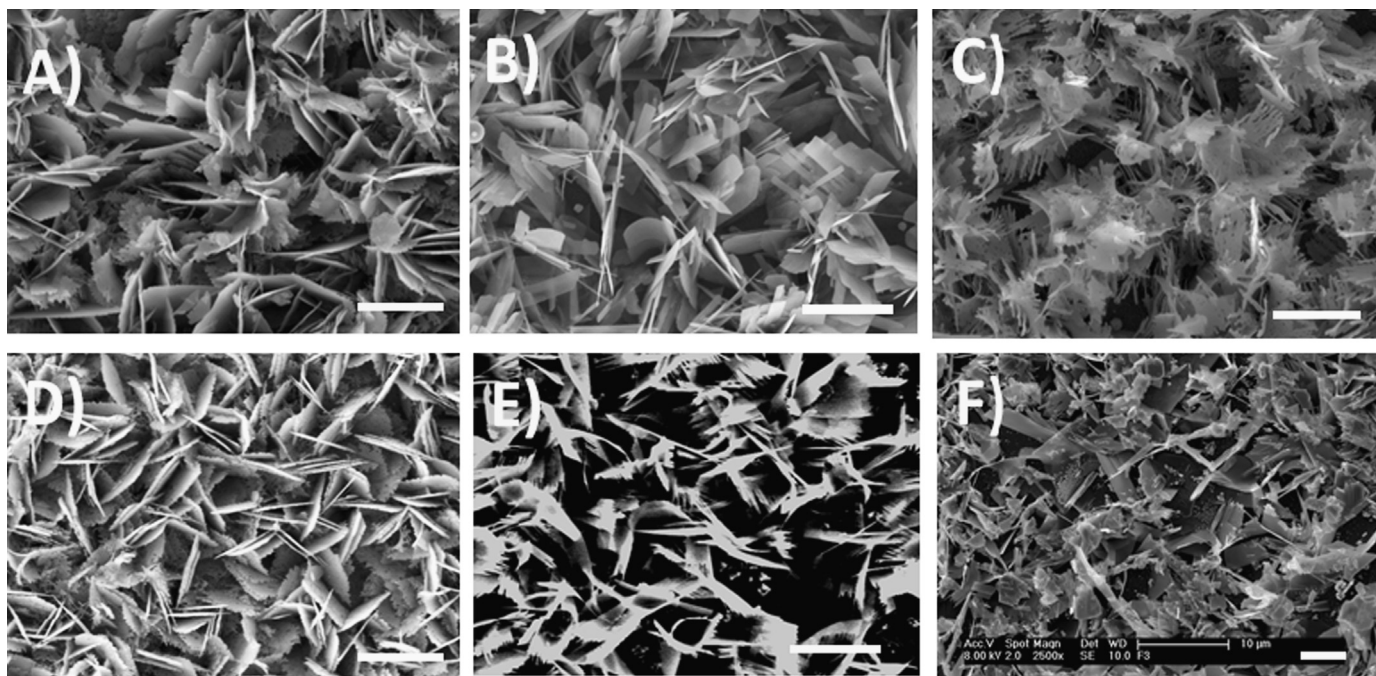


Fig. 7. Secondary electron SEM images of thin films deposited by differing concentrations of precursors (1), (2) or (3) at 450 °C, precursor/amount: (A) (1)/170 mM (B) (1)/250 mM, (C) (2)/170 mM, (D) (2)/250 mM, E) (3) /170 mM, (F) (3)/250 mM. All films were deposited over 45 min. Scale bars: 5 µm.

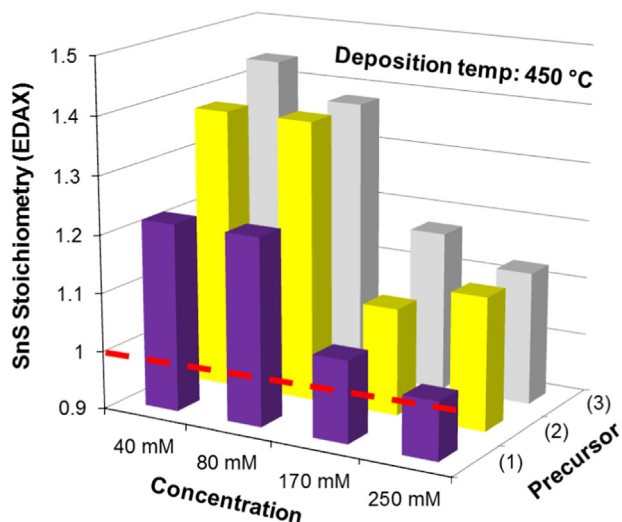


Fig. 8. The effect of concentration of precursors (1)–(3) on the stoichiometry (%Sn divided by %S found experimentally by EDAX) of SnS films deposited at 450 °C by AACVD. The dashed line indicates an ideal 1:1 Sn:S stoichiometry i.e. SnS.

[31]. The increasing band gap energy was attributed to a combination of strain, defects, charged impurities, disorder at grain boundaries and particle size confinement. Contributions from SnO₂ and carbon impurities in the films were not ruled out. Gao et al. prepared SnS films using chemical bath deposition from a mixture of tin(II) chloride, ammonium citrate and sodium thiosulfate at 60 °C and pH 6 which were found to have direct band gaps in the range 1.0–1.3 eV [9]. Bulk SnS is known to have a direct band gap of 1.4 eV [3]. Thus, the orthorhombic SnS film produced by this method from (1) has a direct band gap (1.2 eV) that corresponds well to previously reported films from various deposition routes, including dip deposition (1.4 eV) [21], AACVD (1.2–1.7 eV [31] and 1.2 eV [30]), atmospheric

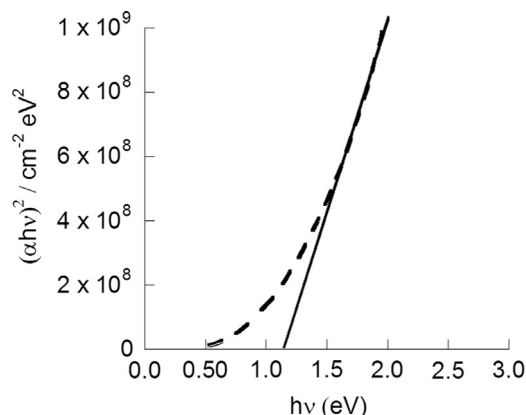


Fig. 9. Determination of the optical band gap for SnS produced by AACVD using precursor (1) (250 mM, 450 °C deposition temperature, 45 min deposition time) by extrapolation of the linear region in $(\alpha h\nu)^2$ as a function of photon energy.

pressure CVD (1.2–1.3 eV) [29], chemical bath deposition (1.0–1.3 eV) [9] and thermal evaporation (1.3 eV) [15] all of which give the same phase of SnS (orthorhombic) and have similar surface morphology, and from their optical band gap are expected to be similar in composition and texture to bulk orthorhombic SnS (1.4 eV).

4. Conclusions

In summary, we report the synthesis unsymmetrical dithiocarbamates of tin(II) of the formula $[\text{Sn}(\text{S}_2\text{CNRR}')_2]$ (where R =ethyl, R' = n -butyl, (1); R =methyl, R' = n -butyl, (2); and $R=R'$ ethyl, (3)) for the deposition of SnS thin films by AACVD. Decomposition of the complexes has been studied using TGA measurements. Tin sulphide (SnS) thin films have been deposited at a range of temperatures by AACVD without an external sulphur source or

co-reagents. SnS was deposited by AACVD using complexes (1)–(3) at 450 or 500 °C with some contamination from SnO₂. AACVD deposition of SnS thin films at 450 °C using precursors (1)–(3) at varying concentrations was studied. The films produced at lower concentrations were moderately contaminated with SnO₂ which at high concentrations reduced to negligible levels as evidenced by p-XRD measurements. SEM combined with EDAX spectroscopy of the SnS films have been used to characterise the structure, morphology and elemental composition of SnS thin films. A direct band gap of ca. 1.2 eV was estimated from optical absorbance measurements of an SnS film of good morphology and composition.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.jcrysgro.2014.07.019>.

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