Chemical vapor deposition of tin sulfide from diorganotin(IV) dixanthates

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ABSTRACT

We report the synthesis and single-crystal X-ray characterization of diphenyltin bis(2-methoxyethylxanthate) and diphenyltin bis(iso-butylxanthate). These xanthates have been used as a single-source precursor to deposit tin chalcogenide thin films by aerosol-assisted chemical vapor deposition. Grazing incidence X-ray diffraction and scanning transmission electron microscope imaging coupled with elemental mapping show that films deposited from diphenyltin bis(iso-butylxanthate) contain orthorhombic SnS, while films deposited from diphenyltin bis(2-methoxyethylxanthate) between 400 and 575 °C form a SnS/SnO2 nanocomposite. In synthesizing the thin films, we have also demonstrated an ability to control the band gap of the materials based on composition and deposition temperature.

Introduction

There has recently been a surge of interest into metal chalcogenide-based materials, as these materials demonstrate a remarkable range of applications including use in magnets, catalysis, lubricants, photovoltaics, energy storage and drug delivery [1–13]. Among these, tin sulfide is a promising material that is suitable as an absorber layer for photovoltaic applications due to its exciting properties. It possesses a high absorption coefficient (α > 10⁴ cm⁻¹) [14], a band gap of 1.1–1.4 eV [15] and a theoretical power conversion efficiency of up to 24%, though so far the record is 4.4%, leaving great room for improvement [16]. It is an attractive material for large scale use, owing to its compositional elements being earth abundant and environmentally benign. SnS in its orthorhombic form demonstrates excellent thermal stability and remains stable under ambient conditions and has found some promise as anodes in Li-ion batteries [17].

Tin is found in the second half of Group 14, and as such has two accessible oxidation states: Sn(II) and Sn(IV). As a result of a fine thermodynamic balance between divalent and tetravalent tin [18], tin sulfide can be found in three main forms: SnS [Sn(II)], Sn2S3 [mixed Sn(II)/Sn(IV)] and SnS2 [Sn(IV)].
energy form of SnS is an orthorhombic herzenbergite structure, adopting a $Pnma$ space group. This is a layered structure with strong Sn–S bonds in a puckered sheet and weak Van der Waals-type interactions between sheets—similar to black phosphorus [19, 20]. The mixed valent species $Sn_2S_3$ also adopts the $Pnma$ space group, while tetravalent $SnS_2$ is trigonal $P-3m1$ [21].

Tin sulfide nanomaterials have been synthesized through a variety of ‘bottom-up’ approaches, such as chemical vapor deposition (CVD) [22–27], chemical vapor transport [28], chemical bath deposition [29, 30], colloidal nanoparticle synthesis [31–33], vacuum vapor deposition [34, 35], physical vapor transport [36], electrochemical deposition [37, 38], spray pyrolysis [39] or ‘top-down’ exfoliation approaches [19]. In most of the ‘bottom-up’ cases, it is difficult to produce phase-pure SnS, with mixtures of $Sn_2S_3$ or $SnS_2$ often found as contaminants.

We have recently focused our attention on the use of single-source precursors to synthesize metal chalcogenide thin films and nanoparticles. In particular, we, and others, have found that simple metal xanthates $[M(S_2COR)x]$ and dithiocarbamates $[M(S_2CNR_2)x]$ (R = alkyl) are excellent precursors to metal sulfides [5, 40–48]. In this report, we discuss the use of the diorganotin(IV) dixanthate complexes as precursors for the production of SnS thin films by aerosol-assisted chemical vapor deposition (AA-CVD). We focus on the annealing temperature and the role of the xanthate ligand during the decomposition process for the potential in controlling the structural and optical properties of the films produced.

**Experimental**

All chemicals were purchased from Sigma-Aldrich and used without further purification. Elemental analysis of the complexes was carried out using a Flash 2000 Thermo Scientific elemental analyzer in the School of Chemistry, University of Manchester. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the complex were carried out by a METTLER TOLEDO TGA/DSC 1 star® system under an atmosphere of dry nitrogen. Scanning electron microscope images (SEM) were observed using a Philips XL 30FEG equipped with DX4 energy-dispersive X-ray spectroscopy (EDX) instrument or a FEI Quanta 200 ESEM equipped with an EDAX Genesis V4.61 for EDX analysis. Grazing incidence X-ray diffraction (GIXRD) patterns were obtained with a Bruker D8 Advance diffractometer using a Cu-Kα source ($\lambda = 1.5418 \, \text{Å}$) and an incident angle of $3^\circ$.

Single-crystal X-ray diffraction was performed using a Bruker APEX-II CCD with a Cu-Kα1 source $[\text{Ph}_2\text{Sn}(\text{S}_2\text{CO}(\text{CH}_2)_2\text{OMe})_2]$ (1) at 100 K and a XtaLAB AFC11 (RINC): quarter-chi single with a Mo–Kα source $[\text{Ph}_2\text{Sn}(\text{S}_2\text{COBu})_2]$ (2) at 150 K.

STEM imaging and energy-dispersive X-ray (EDX) spectroscopic analysis were performed in a probe-side aberration corrected FEI Titan G2 80-200 ChemiSTEM microscope operated at 200 kV equipped with Super-X EDX silicon drift detectors with a total collection solid angle of $\sim 0.7 \, \text{srad}$. For high-angle annular dark-field (HAADF) imaging, a convergence angle of 26 mrad and a detector inner angle of 48 mrad were used. EDX spectrum images were acquired with the sample at 0° tilt and with all four of the ChemiSTEM’s Super-X SDD detectors turned on.

Synthesis of metal xanthate complexes

**Synthesis of potassium 2-methoxyethylxanthate $[KS_2CO(CH_2)_2OMe]$**

Potassium 2-methoxyethylxanthate was prepared according to our previously published procedure [43]. Potassium hydroxide (11.2 g, 0.20 mol) was dissolved in (75 ml) of 2-methoxyethanol, the reactors were stirred for 6 h at 0 °C, and then a solution of $\text{CS}_2$ (15.2 g, 12 ml, 0.20 mol) in 2-methoxyethanol (25 ml) was added dropwise, resulting in a clear yellow solution. $[\text{KS}_2\text{CO}(\text{CH}_2)_2\text{OMe}]$ was isolated from solution by adding THF (100 ml) and shaking the mixture for 15 min. The yellow solid product was dried in vacuo and recrystallized from 2-methoxyethanol to give $[\text{KS}_2\text{CO}(\text{CH}_2)_2\text{OMe}]$ (19.8 g, 0.104 mol, 52% yield). M.p. = 216–219 °C. Calc. for $\text{C}_4\text{H}_7\text{KO}_2\text{S}_2$ (%): C 25.3, H 3.71, S 33.6, K 20.6; found: C 25.5, H 3.79, S 33.5, K 20.8. FT-IR (cm$^{-1}$): 2935 (w), 2888 (w), 1442 (m), 1445 (w), 1230 (m), 1099 (m), 1066 (s), 1018 (m), 844.3 (w), 676.7 (m), 532.5 (m). $^1\text{H}$ NMR (400 MHz, $D_2\text{O}$) $\delta$ (ppm) = 3.35 (s, 3H,
OCH₃), 3.72 (t, 2H, MeOCH₂CH₂OCS₂), 4.50 (t, 2H, MeOCH₂CH₂OCS₂). ¹³C NMR (400 MHz, D₂O) δ (ppm): 58.15 (OCH₃), 70.2 (MeOCH₂CH₂OCS₂), 72.1 (MeOCH₂CH₂OCS₂), 232.5 (MeOCH₂CH₂OCS₂).

Synthesis of potassium iso-butylxanthate [KS₂COBu]

Potassium hydroxide (5.64 g, 0.10 mol) and iso-butanol (50 ml) were stirred for 2 h at room temperature, and then CS₂ (7.73 g, 6.11 ml, 0.10 mol) was added to the reaction, resulting in an orange solution. The unreacted alcohol was removed in vacuo, and the yellow solid product was dried and recrystallized from iso-butanol. (9.66 g, 65% yield). M.p. = 241–243 °C. Calc. for C₈₂H₆₄K₂O₄S₄ (%) C 31.9, H 4.82, S 22.4, K 21.0. FT-IR (cm⁻¹): 2958 (m), 2927 (w), 2870 (w), 1463 (w), 1386 (w), 1362 (w), 1179 (w), 1165 (w), 1092 (s), 937.6 (w), 912.7 (w), 802.1 (w), 653.3 (w), 622.3 (w), 558.2 (w). ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 0.89 (d, 6H, CH(CH₃)₂), 1.99 (s, 1H, CH(CH₃)₂), 4.16 (d, 2H, OCH₂CH)

Synthesis of diphenyltin bis(2-methoxyethylxanthate) [Ph₂Sn(S₂CO(OMe)₂)] (1)

[Ph₂Sn(S₂CO(OMe)₂)] was prepared by a procedure that was modified from that described in the literature [49]. Potassium 2-methoxyethylxanthate [K₂CO(OMe)₂] (0.74 g, 0.0039 mol) in ethanol (50 ml) was added dropwise to a solution of diphenyltin dichloride (0.55 g, 0.0016 mol) in DCM (50 ml) and stirred for 1 h at room temperature. After filtering, the solution was evaporated under reduced pressure and the residue was dissolved in a (1:5) DCM/ethanol solution and left to crystallize as white crystals of [Ph₂Sn(S₂CO(OMe)₂)] (0.62 g, 0.0011 mol, 67% yield). M.p. = 186–189 °C. Calc. for C₃₀H₃₈O₈Sn (%) C 58.3, H 5.48, S 22.1. FT-IR (cm⁻¹): 2958 (m), 2927 (w), 2870 (w), 1463 (w), 1386 (w), 1362 (w), 1179 (w), 1165 (w), 1092 (s), 937.6 (w), 912.7 (w), 802.1 (w), 653.3 (w), 622.3 (w), 558.2 (w). ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 0.89 (d, 6H, CH(CH₃)₂), 1.99 (s, 1H, CH(CH₃)₂), 4.16 (d, 2H, OCH₂CH)

[Ph₂Sn(S₂CO(OMe)₂)] was prepared by the same method using [K(S₂COBu)] (0.73 g, 0.0039 mol). The product crystallizes as needles crystals. (0.58 g, 0.0010 mol, 64% yield). M.p. = 92–94 °C. Calc. for C₃₀H₃₈O₈Sn (%) C 58.3, H 5.48, S 22.1. FT-IR (cm⁻¹): 2958 (m), 2927 (w), 2870 (w), 1463 (w), 1386 (w), 1362 (w), 1179 (w), 1165 (w), 1092 (s), 937.6 (w), 912.7 (w), 802.1 (w), 653.3 (w), 622.3 (w), 558.2 (w). ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 0.89 (d, 6H, CH(CH₃)₂), 1.99 (s, 1H, CH(CH₃)₂), 4.16 (d, 2H, OCH₂CH)

Synthesis of diphenyltin bis(iso-butylxanthate) [Ph₂Sn(S₂COBu)₂] (2)

[Ph₂Sn(S₂COBu)₂] was prepared via the same method using [K(S₂COBu)] (0.73 g, 0.0039 mol). The product crystallizes as needles crystals. (0.58 g, 0.0010 mol, 64% yield). M.p. = 92–94 °C. Calc. for C₃₀H₃₈O₈Sn (%) C 58.3, H 5.48, S 22.1. FT-IR (cm⁻¹): 2958 (m), 2927 (w), 2870 (w), 1463 (w), 1386 (w), 1362 (w), 1179 (w), 1165 (w), 1092 (s), 937.6 (w), 912.7 (w), 802.1 (w), 653.3 (w), 622.3 (w), 558.2 (w). ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 0.89 (d, 6H, CH(CH₃)₂), 1.99 (s, 1H, CH(CH₃)₂), 4.16 (d, 2H, OCH₂CH)

Aerosol-assisted chemical vapor deposition AA-CVD

In a typical deposition of the thin films, 0.25 g, 0.435 mmol of 1 was dissolved in THF (20 ml). A quartz tube reactor containing borosilicate glass substrates (1.8 cm × 1.5 cm × 1 mm thick) was placed in a pre-warmed Carbolite furnace. The precursor solution was aerosolized using an ultrasonic humidifier, and the aerosol droplets were carried to the reactor tube by a constant flow of argon (140 cm³ min⁻¹).

Results and discussion

Diphenyltin bis(2-methoxyethylxanthate) [Ph₂Sn(S₂CO(OMe)₂)] (1, Fig. 1a) and diphenyltin bis(iso-butylxanthate) [Ph₂Sn(S₂COBu)₂] (2, Fig. 1b) were synthesized from the reaction of the corresponding potassium xanthate [43] and diphenyltin dichloride. The free sulfur atoms do not appear to interact with other atoms in the packed structure (ESI Figures S1.1 and S1.2). In 1, the Sn center adopts a distorted tetrahedral arrangement, with Ph–Sn–Ph bond angles of 140.0(2)°–144.2(2)°, S–Sn–S of 86.29(5)°–86.34(5)° and S–Sn–C of 100.6(2)°–104.0(2)°. The Sn–S bond lengths are 2.503(1)–2.543(2) Å, while the non-bonding Sn–S distances are 2.914(1)–3.093(2) Å. Complex 2 adopts an analogous distorted tetrahedral arrangement around the tin center with Ph–Sn–Ph bond angles of 146.7(2)°, S–Sn–S of 86.10(5)° and S–Sn–C of...
It also has similar Sn–S bond lengths to 1 of 2.5065(7)–2.5134(7) Å.

The decomposition of 1 was studied using thermogravimetric analysis (TGA) in the temperature range of 30–600 °C at a heating rate of 10 °C min−1 under nitrogen flow. The TGA trace for 1 (ESI Figure S2.1) shows a clean, one-step decomposition to SnS, with decomposition occurring between 300 and 375 °C. In contrast, 2 undergoes a two-step decomposition to SnS. Metal xanthates typically decompose via the Chugaev elimination mechanism [48], the first step of which involves elimination of the pendant alkyl groups, followed by carbonyl sulfide. The first step of the decomposition of 2 likely involves elimination of 2 equiv. isobutylene and 1 equiv. carbonyl sulfide. The second step would then involve the final loss of the remaining carbonyl sulfide and then aromatic groups. Further investigations will focus on the exact mechanism of decomposition of diaryltin(IV) xanthates.

We used a solution of 1 in THF in an aerosol-assisted chemical vapor deposition (AA-CVD) reactor to generate thin films at temperatures ranging from 400 to 575 °C under an inert atmosphere of Ar. The grazing incidence X-ray diffraction (GIXRD) patterns of the films (Fig. 2a) indicate that at low temperature tetragonal SnO2 (JCPDS 01-070-4177) dominates, but at high temperatures orthorhombic SnS (JCPDS 00-039-0354) is the major species. The GIXRD patterns indicate that at high temperatures some SnO2 is still present, and likewise at low temperature there is still some SnS.

Scanning electron microscopy (SEM) reveals that there is a distinct change in morphology as the deposition temperature is increased (Fig. 3). The particles change from a collection of 0.5 μm cubes to sheets made of thin rods via thin (~ 100 nm) sheets that there is still some SnO2 present at high temperatures and some SnS at low temperatures. 

Figure 1 The structure of a diphenyltin bis(2-methoxyethylxanthate) [Ph₂Sn(S₂CO(CH₂)₂OMe)₂] (1) and b diphenyltin bis(iso-butylxanthate) [Ph₂Sn(S₂COiBu)₂] (2). H are omitted for clarity. Teal = Sn, yellow = S, red = O, gray = C.

Figure 2 a The GIXRD patterns of the obtained films from 1 indicate that tetragonal SnO₂ dominates at low temperatures, but orthorhombic SnS is the major phase at high temperatures. Note that there is still some SnO₂ present at high temperatures and some SnS at low temperatures. b The GIXRD patterns of films obtained from 2 indicate clean formation of SnS at all temperatures.
(Fig. 3). The sulfur composition was determined by energy-dispersive X-ray spectroscopy (EDX, Fig. 3f), and this indicates an increased S content as the reaction temperature is increased. This is in agreement with the GIXRD patterns, which show an analogous transition from SnO$_2$ to SnS.

Samples suitable for transmission electron microscope (TEM) imaging were prepared by ultrasonication of the films deposited at 400 and 575 °C from complex 1. In order to examine the material at higher resolution, high-angle annular dark-field (HAADF) scanning transmission electron microscope (STEM) imaging and STEM-EDX spectrum imaging were used. The microscopy reveals the presence of a possible SnS/SnO$_2$ lateral heterojunction in the material prepared at 575 °C. In Fig. 4a, we show the HAADF STEM image of a sample prepared at 575 °C, which reveals contrasting brighter and darker regions. The EDX maps shown in Fig. 4b–e indicate that the bright regions are oxygen rich, while the darker regions are S rich. An EDX line scan (ESI Figure S3.1) indicates that the S and O are mutually exclusive, with a very sharp transition from SnS to SnO$_2$. It is apparent in this case that the orthorhombic SnS and tetragonal SnO$_2$ are present in the same flake. Atomic resolution TEM images (ESI Figure S3.2) of the material provide further evidence of sharp interfaces between regions of crystalline SnS and SnO$_2$.

In contrast to this, in the sample prepared at 400 °C it appears that SnO$_2$ particles decorate the surface of...
the SnS crystals (Fig. 4f–j). Note that SnS has a density of 5.22 g cm\(^{-3}\), while SnO\(_2\) has a density of 6.95 g cm\(^{-3}\); it is therefore unsurprising that oxide regions appear brighter in HAADF images (Fig. 4f). The sample has a clearly different morphology, appearing much less flake like in the SEM than the other samples (Fig. 3).

The Chugaev elimination usually gives the relevant metal sulfide in a clean manner, with zero O contamination/content [44, 48, 50–54]. We investigated the reason for the presence of SnO\(_2\) in these products through the synthesis and decomposition of a second diorganotin(IV) xanthate, diphenyltin bis(iso-butylanthate) (2, Fig. 1b). 2 was used in the AA-CVD apparatus in exactly the same manner as 1, but in this case the GIXRD pattern indicates that SnS is the only product (Fig. 2b). This result clearly implies that the second oxygen in the xanthate chain of 1 must be key to the production of SnO\(_2\) under the anaerobic conditions of deposition. Therefore, we tentatively suggest that metal alkoxyxanthates of the type \([\text{MS}_2\text{CO(CH}_2\text{OR)}_2]_x\) are a class of compound that is worth further exploration as they may yield interesting and complex MS\(_2\):MO\(_x\) lateral heterojunctions. Alternatively, if seeking to avoid oxide formation, it is clear that the xanthate oxygen is not a problem, but other O atoms further down the alkyl chain are. Future work will look into the ability to fabricate heterostructures from a single molecular precursor: the potential to control both the chemical composition and morphology of the products through reaction temperature is an attractive proposition, especially considering the simplicity and potential scalability of AA-CVD.

The optical band gaps (Eg) of the films were calculated by from Tauc plots (ESI Table S5.1, ESI Figures S5.1 and S5.2). For the films deposited from complex 1, the band gap of the films deposited at 400 °C is 2.97 eV, while increasing the deposition temperature resulted in a decrease in Eg: 2.91 eV (450 °C), 2.60 (500 °C), 2.47 (550 °C) and 1.71 eV (575 °C). SnO\(_2\) is predicted to have direct energy gap of 3.68 eV [55, 56], and SnS has a direct band gap of 1.32 eV [57]. The control of the stoichiometry that we have obtained in the syntheses of the films allows for tuning of band gaps. Films deposited from complex 2 gave pure phase SnS, and the experimentally determined band gaps match the literature values well, with Eg for the films formed at 500, 550 and 575 °C of 1.46, 1.41 and 1.28 eV, respectively.

Conclusions

In conclusion, we have reported the synthesis of SnS thin films and SnS/SnO\(_2\) nanocomposite from diorganotin(IV) xanthate complexes. We have discovered that including a second oxygen in the alkyl chain of the xanthate can be used to introduce an certain amount of oxide formation, with the stoichiometry being controllable through deposition temperature. The method that we have presented
here is simple and easily scalable, which we hope will encourage the use of this exciting material. We believe that this control over the stoichiometry of oxide to chalcogenide may be of use to researchers looking at other metal chalcogenides/oxides, with the potential for synthesizing lateral heterostructures. This could access exciting functionality and thus increase the abilities of future devices.

Acknowledgements

The authors would like to acknowledge the Iraqi Culture Attaché in London and Department of Physics, College of Science, University of Misan, Iraq, for financial support (M.A.S.) and the EPSRC (Doctoral Prize for E.A.L., Grant EP/M507969/1). Some of the equipments used in this study were provided by the Engineering and Physical Sciences Research Council (Core Capability in Chemistry, EPSRC Grant Number EP/K039547/1). P.D.M. would like to acknowledge the UK Government and European Union as contributors to the Smart Energy Network Demonstrator (ERDF Project Number 32R16P00706).

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Electronic supplementary material: The online version of this article (https://doi.org/10.1007/s10853-018-2968-y) contains supplementary material, which is available to authorized users.

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