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The first single source deposition of tin sulfide coatings on glass: aerosol-assisted chemical vapour deposition using $[Sn(SCH_2CH_2S)_2]$

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Aerosol-assisted chemical vapour deposition of SnS has been achieved on glass substrates from the single source precursor $[Sn(SCH_2CH_2S)_2]$ at 400–550 °C. In the presence of H_2S the precursor produces films of SnS_2 at 350 °C, Sn_2S_3 at 400 °C and SnS at 500 °C. The tin sulfides were analysed by Raman (SnS_2 312 and 215 cm^{-1}; Sn_2S_3 307, 251, 234, 183, 87, 71, 60, 52 and 36 cm^{-1} and SnS 288, 220, 189, 163 and 96 cm^{-1}), EDAX, SEM and band gap measurements (SnS 1.15 eV, SnS_2 2.20 eV). Growth rates were of the order of 15 nm min^{-1}.

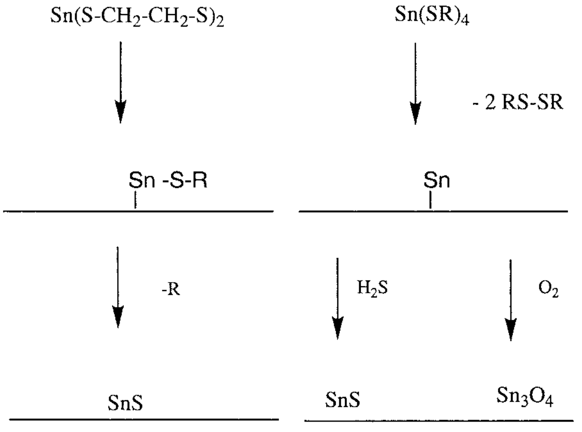
Introduction

Tin forms three main sulfides, SnS_2, Sn_2S_3 and SnS.[1] The most important of these, SnS (1.3 eV) and SnS_2 (2.18 eV), have band gaps that are close to Si (1.12 eV) and GaAs (1.43 eV).[2] Thin films of tin(II) and tin(IV) sulfides have been investigated as semiconductors, solar collectors and photovoltaic materials with high energy conversion.[3] Tin monosulfide adopts a distorted GeS structure in which each tin atom is coordinated by six sulfur atoms.[4] The bond distance variation is explained by the layer structure and a stereochemically significant s–p hybridised lone pair on the tin atoms.[4] Tin(IV) sulfide has in excess of seventy polytype structures based on hexagonal close packed layers similar to that adopted by PbI_2.[1]

Tin sulfides have been synthesised in bulk by solid state metathesis,[5] elemental combination reactions at high temperature,[6] reactions in ammonia[7] and n-butylamine,[8] decomposition of molecular precursor templates such as $(Ph_2SnS)_3$[9] and by the reaction of H_2S on the metal oxide. Thin films of tin sulfides have been produced by spray pyrolysis,[10] chemical baths,[11] electrodeless deposition[12] and vapour transport methods.[13] Until recently there were only limited reports on the low pressure CVD of tin sulfides from organometallic precursors and plasma enhanced CVD. The organometallic routes produced yellow and grey films on CaF_2 and MgF_2 substrates at 600 °C from reactions of $SnEt_4$ with H_2S and H_2.[14] These films were speculated to be SnS purely on the reducing conditions employed and were not spectroscopically characterised. Plasma enhanced CVD has enabled SnS to be obtained from reaction of tin tetrahalides and H_2S, however the products were contaminated with chlorine.[15]

We have instigated a systematic atmospheric pressure CVD study of tin sulfides on glass substrates using a cold-wall static coater. Our initial studies centred on the dual-source reaction of SnX_4 (X = Br, Cl) or other volatile organotins (*e.g.* $Bu_3SnO_2CCF_3$) with H_2S.[16] All systems promoted conformal uniform coverage of large glass plates (21 × 9 cm). The phases of tin sulfide deposited under these conditions were found to be highly dependent on the substrate temperature, such that SnS_2 was formed from 300–500 °C, Sn_2S_3 at 525 °C and at 545 °C and above single phase SnS was observed.[16] Our next goal was to produce single source precursors to tin sulfide coatings and a range of precursors [*e.g.* $Sn(SCH_2CF_3)_4$, $Sn(SPh)_4$, $Sn(SCy)_4$] have been investigated by both AACVD and APCVD.[17] In all of these systems, tin oxide Sn_3O_4 was the dominant phase produced in the absence of H_2S. However, under a partial pressure of H_2S (1% of gas stream) SnS and SnS_2 could be obtained.[17] The reason for the formation of tin oxides was unexpected as the precursors were oxygen free and the glass substrates had a SiCO barrier layer to stop oxygen diffusion from the glass. We speculated that the oxygen came from the nitrogen carrier gas used in the reactions. In the homoleptic tin(IV) thiolate complexes $[Sn(SR)_4]$ a facile mechanism exists for the elimination of the disulfide RS–SR. This mechanism is backed up by thermogravimetric analysis and mass spectrometry data that show that $[Sn(SR)_4]$ predominantly forms RS–SR in the gas phase. In other work using $[Sn(SR)_n(SeR)_{4-n}]$ the elimination of RS–SeR is less favoured presumably because of the lower heteroleptic chalcogenide bond energy and this has enabled a partial SnS_xSe_y coating to be obtained in the absence of H_2S.[18] It is thus probable that $[Sn(SR)_4]$ precursors undergo a double disulfide elimination to form tin metal which then reacts with either traces of oxygen gas to form Sn_3O_4 or with a partial pressure of H_2S to form SnS (Scheme 1).

The formation of post transition-metal chalcogenide coatings by LPCVD and by chemical-bath methods has been



Scheme 1 Probable deposition pathway for chelating thiolates and monodentate thiolates on tin. The monodentate species undergo a disulfide elimination pathway forming tin metal on the surface that forms either tin oxide in the presence of oxygen or tin sulfide if in the presence of H_2S.

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demonstrated by O'Brien and coworkers who have formed a series of PbS, CdS and ZnS coatings.[19] The ligands chosen for these reactions were chelating diseleno- and dithiocarbamates. These ligands proved to be very versatile forming coatings from a liquid injection method and by LPCVD, where the unsymmetric dithiocarbamates were shown to have superior volatility and film growth characteristics. Notably coatings could be grown in all cases without recourse to an ancillary sulfur source.

In order to try and alleviate the requirement of using H_2S in the deposition process and to develop the single-source approach to forming tin sulfide thin films, we report here the use of chelating thiolate ligands which would be anticipated to significantly hinder the disulfide elimination pathway.

Experimental

Nitrogen (99.99%) and H_2S (99.9%) were obtained by BOC and used as supplied. Coatings were produced on SiCO coated glass. Deposition experiments were conducted on 225 × 89 × 4 mm glass pieces using a horizontal-bed cold wall reactor. The glass was cleaned by washing with petroleum ether (bp 60–80 °C) 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 in internal diameter except for the inlet to the mixing chamber and the exhaust line from the apparatus which were 1/2 in i.d. In these experiments two gas lines were used, one for nitrogen and one for a hydrogen sulfide line. The gases came directly from a cylinder. An aerosol of $Sn(SCH_2CH_2S)_2$ (0.1 g) in 50 ml acetone was generated by a PIFCO HEALTH ultrasonic humidifier (product no 1077). The nitrogen/H_2S gas streams were introduced into the aerosol vapour and used to carry the vapour into the reactor. Gas flows were adjusted using suitable regulators (Spectrol 50S for the H_2S 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 each run. Deposition experiments were conducted by heating the horizontal-bed reactor to the required temperatures before diverting the nitrogen line through the aerosol and hence to the reactor (Table 1). Deposition experiments were timed by stopwatch and were typically 20 minutes. 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 *ca.* 60 °C before it was removed. Coated substrates were handled and stored in air. The large coated glass sample was broken up into *ca.* 1 cm × 1 cm squares for subsequent analysis by EDAX, SEM and UV studies. Large pieces of glass (*ca.* 4 cm × 4 cm) were used for sheet resistance, X-ray powder diffraction, Raman and Scotch-tape tests.

Table 1 Deposition conditions and analysis of the films grown from the AACVD of $[Sn(SCH_2CH_2)_2]$

Coater temperature/°C	H_2S flow rate/ $dm^3\ min^{-1}$	SEM morphology	EDAX	Raman
350	0	No coating	No coating	No coating
400	0	Angular particles	Yes	SnS $+[Sn_2S_3]$
410	0	Angular particles	Yes	SnS
450	0	Square particles	Yes	SnS
490	0	Square particles	Yes	SnS
500	0	Square particles	—	SnS
350	0.2	Round particles	Yes	SnS_2
400	0.2	Needles	—	Sn_2S_3
410	0.2	Needles + square particles	Yes	Sn_2S_3 + SnS
500	0.2	Square particles	Yes	SnS
550	0.2	Square particles	Yes	SnS

X-Ray powder diffraction patterns were measured on a Philips X-pert diffractometer using unfiltered CuK_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 results were 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.

All synthetic manipulations were carried out under an anaerobic argon atmosphere. THF was distilled over Na/benzophenone prior to use; CH_2Cl_2 was distilled over CaH_2 prior to use. Ethane-1,2-dithiol, n-BuLi solution and $SnCl_4$ were commercially obtained and used without further purification.

Synthesis of $[Sn(SCH_2CH_2S)_2]$ 1[20]

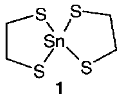
To a stirred solution of ethane-1,2-dithiol (1.45 cm^3, 17.2 mmol) in THF (50 cm^3) was added 2.5 M n-BuLi in hexanes (13.7 cm^3, 34.2 mmol) causing the formation of a white precipitate. This suspension was stirred at room temperature for 30 min prior to dropwise addition of $SnCl_4$ (1.0 cm^3, 8.55 mmol), causing an exothermic reaction. After stirring for 16 h, the THF was removed *in vacuo* and replaced with CH_2Cl_2 (40 cm^3). Insoluble LiCl was removed by filtration and the solvent removed from the filtrate *in vacuo*, leaving the desired product as a white powder (2.36 g, 91%, mp 180–181 °C, lit. 178 °C,[21] 182 °C[22]). The product was determined by NMR to be identical to a previously reported sample.[22]

Analysis, found (calc. for $C_4H_8S_4Sn$): C 15.9 (15.8), H 2.59 (2.64)%.

Results

Reaction of $Sn(SCH_2CH_2S)_2$ with H_2S under AACVD conditions

Reaction of $[Sn(SCH_2CH_2S)_2]$ **1** with H_2S under aerosol-assisted CVD (AACVD) conditions on glass substrates produces thin films of tin sulfides (Table 1). The phase of tin sulfide deposited on the glass was dependent on the deposition temperature; at 350 °C a yellow SnS_2 coating was formed, at 400 °C a brown coating of Sn_2S_3 and at 500 °C and above a grey-silver coating of SnS was formed. A deposition time of 20 minutes for all runs was sufficient to produce a coating adequate for analysis. AACVD conditions were necessary as the precursor was involatile and gave poor carry-over by APCVD. The AACVD technique also has the advantage of requiring only minimal amounts of precursor (*ca.* 0.1 g per run).



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Film analysis

The films produced by **1** with H_2S under AACVD conditions were characterised by Raman, X-ray powder diffraction, SEM/EDAX, optical measurements and surface adherence Scotch-tape tests. All of the films were shown to be X-ray amorphous, which is probably in part a consequence of the film thickness (*ca.* 300 nm) which leads to a featureless diffraction pattern. EDAX showed that all of the films contained tin and sulfur, with elemental ratios that were in agreement with the ratios expected for the films. However significant breakthrough of the excitation volume through the coating to the underlying glass meant that accurate quantitative analysis was difficult. All of the films passed the Scotch-tape test but could be abraded with a paper towel. The morphology of the films was dependent on the deposition temperature. At 350 °C the films were made up of rounded particles of dimension 300 nm corresponding to SnS_2, at 400 °C the needle-like morphology characteristic of Sn_2S_3 was observed (Fig. 1a) whilst at 500 °C overlapping square plates *ca.* 2 μm × 2 μm were seen (Fig. 1b). SEM analysis indicates that the films were *ca.* 300 nm thick. We have previously reported the Raman patterns of tin sulfides on glass from reactions of H_2S and $SnCl_4$.[16] These spectra have proven to be highly diagnostic of the material formed, *i.e.*, SnS_2 shows two bands at 312 and 215 cm^{-1}; Sn_2S_3 shows bands at 307, 251, 234, 183, 87, 71, 60, 52 and 36 cm^{-1} and SnS bands at 288, 220, 189, 163 and 96 cm^{-1}. In the AACVD reaction of $[Sn(SCH_2CH_2)_2]$ with H_2S, SnS_2 was identified in films obtained at 350 °C, Sn_2S_3 from the films at 400 °C and SnS from the films obtained at 500 °C and above (Fig. 2). The colours of the films are also somewhat diagnostic, and were consistent with previous work on glass substrates which has shown that SnS_2 films are yellow, Sn_2S_3 brown and SnS a silver-grey. These colours are also consistent with the Raman analysis and EDAX results obtained from the AACVD reaction of $[Sn(SCH_2CH_2S)_2]$ with H_2S. The optical properties of the SnS films gave direct band gaps of 1.15–1.16 eV, and for SnS_2 films at 2.20 eV which compare well with literature measurements (1.2–1.3 eV and 2.20 eV).[2]

Reaction of $Sn(SCH_2CH_2S)_2$ without H_2S under AACVD conditions

Reaction of **1** under AACVD conditions without the use of H_2S also leads to the formation of tin sulfide films. At 350 °C and below no film could be grown from this system, at 400 °C yellow-grey films containing SnS and a trace of Sn_2S_3 were obtained whilst at 500 °C and above single-phase SnS was obtained (Table 1). A deposition time of 20 minutes was again adequate to produce coatings thick enough for analysis.

Characterisation

The films produced from the single-source AACVD process utilising **1** were characterised in the same manner to those outlined above. The films were *ca.* 200 nm in thickness and X-ray amorphous. The Sn_2S_3 was present as a minor phase by Raman, however the SEM showed angular particles rather than the needle-like particles grown in the presence of H_2S. The SnS films were characterised by Raman and EDAX and showed good agreement with previous literature measurements.[16] SEM showed overlapping square plates of dimension *ca.* 1–2 μm (Fig. 1c). All the films produced passed the Scotch-tape test but could be abraded with a scalpel. The SnS films showed similar direct band gaps to literature values (1.20 eV).[2]

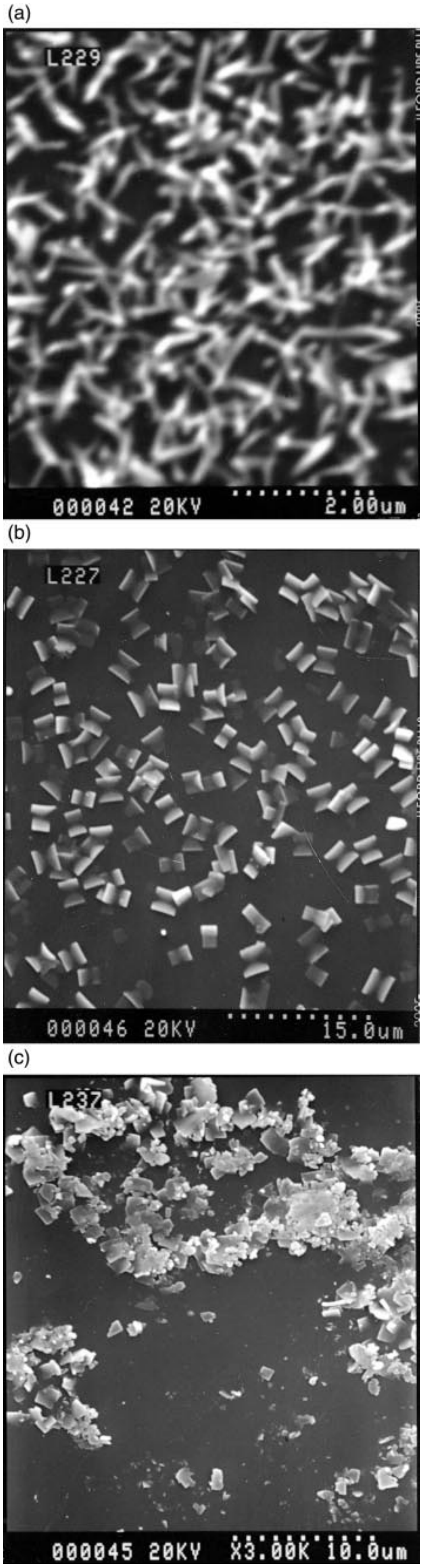

Fig. 1 (a) SEM micrograph of Sn_2S_3 grown from the AACVD of $[Sn(SCH_2CH_2S)_2]$ and H_2S at 400 °C. (b) SEM micrograph* of SnS grown from the AACVD of $[Sn(SCH_2CH_2S)_2]$ and H_2S at 500 °C. (c) SEM micrograph* of SnS grown from the AACVD of $[Sn(SCH_2CH_2S)_2]$ without H_2S at 500 °C. (* far-edge region of plate shown to emphasise particle morphology).

Discussion

The synthesis[20,21] and structure[19,20] of $[Sn(SCH_2CH_2S)_2]$ **1** have been described by others. The high melting point of the material can be ascribed to weak intermolecular S···Sn interactions [3.752, 3.791,[19] 3.764 and 3.811 Å] evident in the solid state structure. As such, conventional CVD methodology was not attempted due to the inherent low volatility of the precursor. In such circumstances aerosol-assisted CVD provides an active alternative, enabling films to be grown from minimal amounts of precursor, with growth rates in excess of those obtained by low pressure CVD.

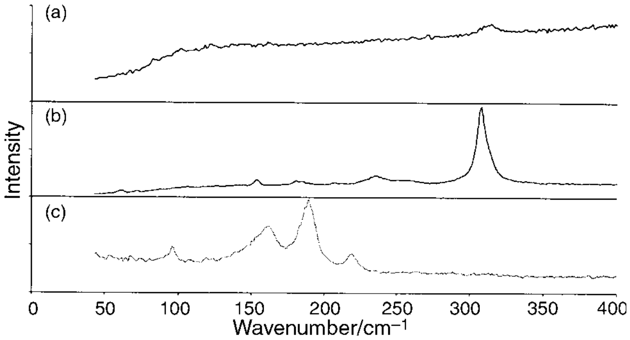

Fig. 2 Raman pattern for the films grown from the AACVD of $[Sn(SCH_2CH_2S)_2]$ and H_2S at a) 350 °C (SnS_2); b) 400 °C (Sn_2S_3) and c) 500 °C (SnS).

Reaction of **1** under AACVD conditions in acetone solvent, with or without the presence of H_2S, formed tin sulfide films. The reactions in the presence of H_2S formed a more sulfur-rich tin film, with SnS_2 being formed at 350 °C; Sn_2S_3 at 400 °C and SnS at 500 °C and above. This pattern has been observed for a wide range of APCVD experiments where dual-source reagents were employed; tin sources have included $[SnCl_4]$, $[SnBr_4]$, $[Sn(SCH_2CF_3)_4]$, $[SnBu_3O_2CCF_3]$ and $[Sn(SPh)_4]$, whilst the sulfur source in all the systems was H_2S.[16] The temperature change-over between the specific phase deposited (SnS_2, Sn_2S_3 and SnS) varied by *ca.* 100 °C depending on the precursor employed.

We have noted previously that tin derivatives of monothiolate ligands, *e.g.* $(PhS)_4Sn$, decompose by disulfide elimination to leave reactive tin metal, which is readily oxidised to Sn_3O_4 in the absence of added H_2S (Scheme 1).[16] The use of a chelating bis-thiolate in the title compound obviates the possibility of this occurring; hence its successful use as a single-source precursor for tin sulfide films.

The EI mass spectrum of $Sn(SCH_2CH_2S)_2$ contains a strong parent ion (35%) along with fragments due to $Sn(SCH_2CH_2S)$ (10%) and SCH_2CH_2S (100%). However, fragments at 184 (SnS_2; 15%) and 152 (SnS; 7%) show that fragmentation by a mechanism other than complete ligand loss can occur. The only other tin-containing fragment in the mass spectrum occurs at 245 (6%) and corresponds to $Sn(SCH_2CH_2S)(SH)$, showing that elimination of the hydrocarbon groups can occur with retention of the Sn–S bond. Little mechanistic information can be gained from the TGA. The primary decomposition takes place in a single step between 250–375 °C with *ca.* 45% weight loss. This exceeds the amount expected for the formation of SnS_2 (40%) suggesting that the precursor has some volatility. A further 10% weight loss between 500–550 °C corresponds to the formation of SnS.

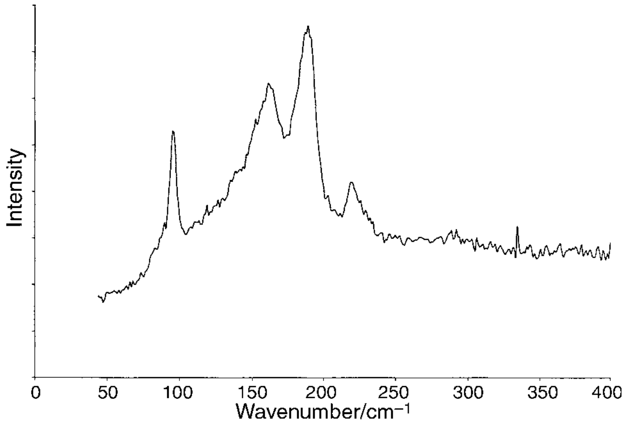

Fig. 3 Raman patterns for the film grown from the AACVD of $[Sn(SCH_2CH_2S)_2]$ at 450 °C (SnS).

Reaction of **1** under AACVD conditions without the presence of H_2S did lead to the formation of tin sulfide films. At 400 °C a mixed phase of SnS with a minor component of Sn_2S_3 was observed, whilst at 450 °C and above phase-pure SnS was produced (Fig. 3). This is to our knowledge the first time that a single-source precursor has led to the formation of tin sulfide films, in contrast to other single-source precursors such as $[Sn(SCH_2CF_3)_4]$ and $[Sn(SPh)_4]$.[16] In all cases in the absence of a secondary sulfur source such as H_2S the precursors failed to produce tin sulfide films and either no film was obtained from the reaction or a tin oxide film was produced.

Mass spectrometry studies of the non chelated tin thiolate precursors show that the predominant species in the gas phase is the disulfide, *e.g.* in the case of $[Sn(SPh)_4]$ this was PhS–SPh; no parent ion was observed. It would appear likely that despite having the required Sn–S bond in the precursor this is lost during the CVD process, which either produces no coating or leaves a thin film of tin on the glass surface. This thin film of tin can be readily oxidised, probably from the residual oxygen in the nitrogen stream, to form a tin oxide coating. If H_2S is added to the gas streams even at relatively low levels (1–10% of gas flow), tin sulfide films can be readily produced from these tin thiolate precursors. The H_2S either interacts with the tin species in the gas phase to promote tin sulfide formation or it could react with the tin deposited on the surface to form a tin sulfide coating (Scheme 1). Notably, we have shown that tin oxide coatings are readily converted to tin sulfides under APCVD conditions. In the set of experiments reported here the chelating tin thiolate $[Sn(SCH_2CH_2S)_2]$ does, for the first time, afford a single-source precursor route to tin sulfide films. The chelate effect of the bis-thiolate ligand appears, as evidenced from mass spectometry studies, to suppress the disulfide elimination mechanism and enables tin sulfide films to be produced from a single compound.

Conclusions

Tin sulfide thin films can be grown from single-source precursors by taking advantage of the chelate effect which suppresses decomposition *via* disulfide elimination, which is prevalent when compounds in which tin is ligated by monodentate thiolates are employed. This has enabled the first single-source precursor route to tin sulfide films. The tin sulfide films show equivalent properties to bulk material, including band gap measurements. The AACVD method is readily applicable to the formation of thin films from minimal amounts of precursor (0.1 g).

Acknowledgements

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References

1 T. Jiang and G. Ozin, *J. Mater. Chem.*, 1998, **8**, 1099.
2 S. K. Arora, D. H. Patel and M. K. Agarwal, *J. Mater. Sci.*, 1994, **29**, 3979; A. Ortiz, J. C. Alonso, M. Garcia and J. Toriz, *Semicond. Sci. Technol.*, 1996, **11**, 243; U. V. Alpen, J. Fenner and E. Gmelin, *Mater. Res. Bull.*, 1975, **10**, 175.
3 M. Radot, *Phys. Appl.*, 1977, **18**, 345; J. P. Singh and R. K. Bedi, *Thin Solid Films*, 1991, **199**, 9; P. K. Nair, M. T. S. Nair, A. Fernandez and M. Ocampo, *J. Phys. D: Appl. Phys.*, 1989, **22**, 829.
4 I. P. Parkin and A. T. Rowley, *Polyhedron*, 1993, **12**, 2961.
5 R. Coustal, *J. Chim. Phys.*, 1931, **31**, 277.
6 G. Shaw and I. P. Parkin, *Main Group. Met. Chem.*, 1996, **19**, 499; G. Henshaw, I. P. Parkin and G. Shaw, *J. Chem. Soc., Dalton Trans.*, 1997, 231.
7 V. Dusastre, B. Omar, I. P. Parkin and G. A. Shaw, *J. Chem Soc., Dalton Trans.*, 1997, 3505.

8 P. Boudjouk, S. R. Bahr and G. J. McCarthy, *Chem. Mater.*, 1992, **4**, 383; P. Boudjouk, D. J. Seidler, S. R. Bahr and G. J. McCarthy, *Chem. Mater.*, 1994, **6**, 2108.

9 Y. M. Gao, P. Wu, J. Baglio, K. M. Dwight and A. Wold, *Mater. Res. Bull.*, 1989, **24**, 1215.

10 A. Ortiz and S. Lopez, *Semicond. Sci. Technol.*, 1994, **9**, 2130.

11 R. D. Engleken, H. E. McCloud, C. Lee, M. Slayton and H. Ghoreishi, *J. Electrochem. Soc.*, 1987, **134**, 2696.

12 M. T. S. Nair and P. K. Nair, *Semicond. Sci. Technol.*, 1991, **6**, 132.

13 H. P. B. Rimmington and A. A. Balchin, *J. Cryst. Growth.*, 1972, **15**, 51; S. K. Arora, D. H. Patel and M. K. Agarwal, *J. Mater. Sci. Lett.*, 1994, **29**, 3971.

14 H. M. Manasevit and W. I. Simpson, *J. Electrochem. Soc.*, 1975, **122**, 444.

15 A. Ortiz, J. C. Alonso, M. Garcia and J. Toriz, *Semicond. Sci. Technol.*, 1996, **11**, 243.

16 L. S. Price, I. P. Parkin, A. M. E. Hardy, R. J. H. Clark, T. G. Hibbert and K. C. Molloy, *Chem. Mater.*, 1999, **11**, 1792; L. S. Price, I. P. Parkin, T. G. Hibbert and K. C. Molloy, *Chem. Vap. Deposit.*, 1998, **4**, 222; I. P. Parkin, L. S. Price, A. M. E. Hardy, R. J. H. Clark, T. G. Hibbert and K. C. Molloy, *J. Phys. IV France*, 1999, **9**, 403; L. S. Price, I. P. Parkin, M. N. Field, A. M. Hardy, R. J. H. Clark, T. G. Hibbert and K. C. Molloy, *J. Mater. Chem.*, 2000, **10**, 527.

17 T. G. Hibbert, M. F. Mahon, K. C. Molloy, L. S. Price and I. P. Parkin, *J. Mater. Chem.*, 2001, **11**, 464; G. Barone, T. G. Hibbert, M. F. Mahon, K. C. Molloy, L. S. Price, I. P. Parkin, A. M. E. Hardy and M. N. Field, *J. Mater. Chem.*, 2001, **11**, 469.

18 P. Parkin, L. S. Price, A. M. E. Hardy, R. J. H. Clark, T. G. Hibbert and K. C. Molloy, unpublished results.

19 M. Motivalli, P. O'Brien, J. R. Waals and I. M. Watson, *Polyhedron*, 1996, **15**, 2801; M. A. Malik, M. Motivall, T. Saeed and P. O'Brien, *Adv. Mater.*, 1993, **5**, 653; M. A. Malik and P. O'Brien, *Chem. Vap. Deposit.*, 1997, **3**, 75.

20 A. G. Davies, S. D. Slater, D. C. Povey and G. W. Smith, *J. Organomet. Chem.*, 1988, **352**, 283.

21 R. C. Poller and J. A. Spillman, *J. Chem. Soc. A*, 1966, 958.

22 P. A. Bates, M. B. Hursthouse, A. G. Davies and S. D. Slater, *J. Organomet. Chem.*, 1989, **363**, 45.