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Deposition of tin sulfide thin films from novel, volatile (fluoroalkythiolato)tin(IV) precursors

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Novel, volatile (fluoroalkylthiolato)tin(IV) precursors have been synthesised and $(CF_3CH_2S)_4Sn$ used to deposit tin sulfide films under APCVD (atmospheric pressure chemical vapour deposition) conditions. H_2S is, however, required as co-reactant. Films deposited at 300–400 °C are composed of sulfur-deficient SnS_2, films deposited at 450 and 500 °C comprise the sesquisulfide, Sn_2S_3, and the films deposited at 550 or 600 °C are sulfur-deficient SnS. The structure of $[CF_3(CF_2)_5CH_2CH_2S]_4Sn$ is also reported.

1. Introduction

Three common tin sulfides are known with differing band gaps: yellow SnS_2 (2.18 eV),[1] grey SnS (1.3 eV)[2] and brown Sn_2S_3 (0.35 eV).[3] Thin films of these sulfides have potentially diverse applications as holographic recording media,[4,5] in solar collectors,[2] as photovoltaic materials with high conversion efficiency[6] and solar control coatings.[7] We have been interested in chemical vapour deposition (CVD) routes to these materials, to complement more extensive work on the synthesis of bulk materials.[8–13] Previous work from our groups has shown that all three tin sulfides can be deposited from SnX_4 and H_2S (X = Cl,[14,15] Br[16]) by suitable control of deposition temperature. Other precursors can be used in this dual-source approach *e.g.* $Bu_3SnO_2CCF_3$.[17] Surprisingly, tin thiolates such as $(PhS)_4Sn$ also require H_2S to generate tin sulfide films, with Sn_3O_4 being deposited in the absence of H_2S.[18] In addition, $(PhS)_4Sn$ proved too involatile for conventional atmospheric pressure CVD (APCVD) and films were deposited using an aerosol-assisted methodology (AACVD). Other methods of depositing tin sulfides are fully documented in our previous papers.[15]

In this paper we report the synthesis and characterisation of fluorinated tin thiolates and the use of the most volatile species, $(CF_3CH_2S)_4Sn$, for the APCVD of tin sulfide films.

2. Experimental

Instrumentation

Infrared spectra (cm^{-1}) were recorded as hexachlorobutadiene mulls between KBr plates, unless stated otherwise. Measurements were made using a Nicolet 510P Fourier transform spectrometer within the range 4000–400 cm^{-1} with a medium slit width and a peak resolution of 4.0 cm^{-1}. Carbon, hydrogen and nitrogen were determined using a Carlo-Erba Strumentazione E.A. model 1106 microanalyser operating at 500 °C; results were calibrated against an acetanilide standard. ^1H and ^{13}C NMR spectra were recorded as C_6D_6 solutions using either Jeol JNM-GX-270FT (270 MHz) or Jeol EX-400 (400 MHz) Fourier transform spectrometers with $SiMe_4$ as an internal reference. ^{19}F and ^{119}Sn NMR spectra were recorded on a Jeol EX-400 (400 MHz) spectrometer; chemical shifts are in ppm relative to Me_4Sn or $CFCl_3$. Details of our Mössbauer spectrometer and data handling procedures are given elsewhere.[19]

Raman spectroscopy was carried out on a Renishaw System 1000 Raman spectrometer using a Renishaw HeNe laser with an air-cooled CCD detector coupled to a Leica microscope. Spectra were calibrated using neon emission lines. X-Ray diffraction was carried out on a Philips XPert diffractometer using Cu-K_α radiation in the reflection mode. PC-APD version 4.0b software was used to control the diffractometer and UnitCell[20] to index the patterns. SEM and EDAX were obtained using a Hitachi S570 scanning electron microscope with a beryllium window and an excitation energy of 20 kV. EDAX analyses were quantified using the Oxford Instruments AM10,000 software package and standardised relative to cobalt metal. X-Ray photoelectron spectroscopy was carried out on a VG ESCALAB 220I XL instrument using monochromatic Al-K_α radiation at a pass energy of 20 eV and a spot size of 600 μm. Samples were etched with an Ar^+ ion gun.

Synthesis

All synthetic manipulations were carried out under an atmosphere of dry nitrogen. Toluene was distilled over sodium wire prior to use. All other chemicals were commercially obtained and using without further purification.

$[CF_3(CF_2)_5CH_2CH_2S]_4Sn$ 1. $CF_3(CF_2)_5CH_2CH_2SH$ (6.50 g, 17.1 mmol) was dissolved in toluene (100 ml) and $SnCl_4$ (0.5 ml, 4.28 mmol) added dropwise. Ammonia was then bubbled slowly through the reaction mixture, causing a white precipitate of NH_4Cl. This bubbling was continued until no more precipitate was formed. The NH_4Cl was removed by filtration and then toluene removed *in vacuo*. Recrystallisation of the remaining white solid from ether gave colourless crystals of **1**·1/2NH_3 (6.47 g, 92%; mp 37 °C). Analysis: found (calculated for $C_{32}H_{17.5}F_{52}N_{0.5}S_4Sn$) C 23.1(23.4), H 1.04(1.08), N 0.39(0.43)%. ^1H NMR: 2.20 (8H, m, CH_2S), 2.83 (8H, m, CF_2CH_2); ^{13}C NMR: 30.9 (CH_2S), 31.9 (m, CH_2CF_2), 111.2 (m, 5 × CF_2), 118.9 (m, CF_3); ^{19}F NMR: −83.2 (2F, m), −115.9 (2F, m), −122.4 (2F, m), −123.5 (3F, m), −124.8 (2F, m) −128.1 (2F, m); ^{119}Sn NMR: 145.0 ppm; IR: 2926s 1459s 1377m 1253m 1202m 1139s 1084m 954m 734s 708s 642m cm^{-1}; Mössbauer: IS = 0.01, QS = 0.74 mm s^{-1}.

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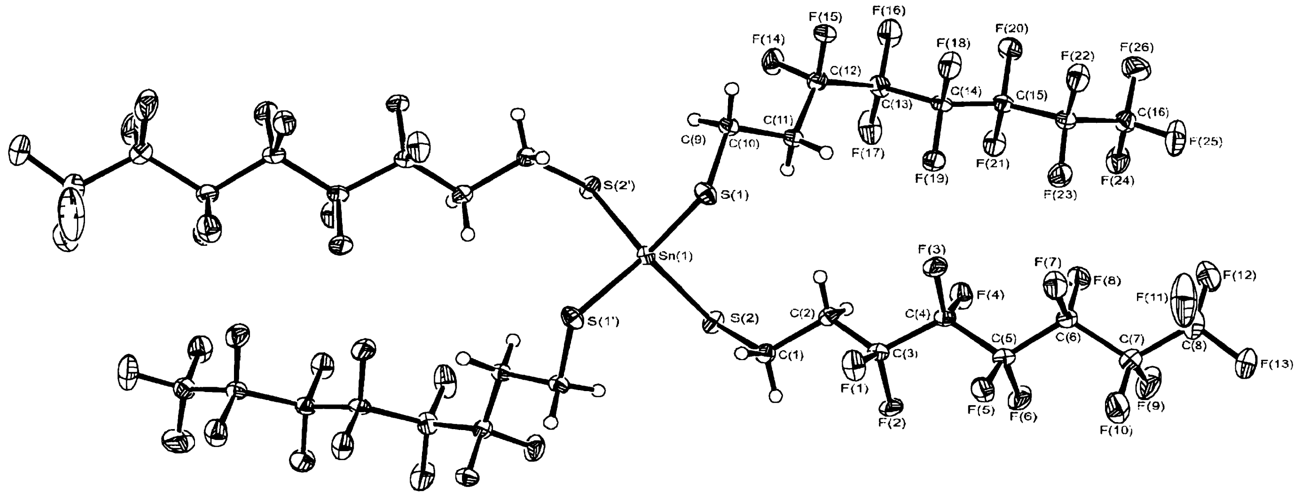

Fig. 1 ORTEX[34] plot of the asymmetric unit of **1**. Selected metrical data: Sn(1)–S(1) 2.3960(9), Sn(1)–S(2) 2.3817(9), S(1)–C(9) 1.834(3), S(2)–C(1) 1.836(3); S(2′)1–Sn(1)–S(2) 110.74(4), S(2)–Sn(1)–S(1) 113.17(3), S(2)–Sn(1)–S(1′) 108.38(3), S(1′)–Sn(1)–S(1) 102.84(4), C(9)–S(1)–Sn(1) 101.3 (1), C(1)–S(2)–Sn(1) 99.5(1).

[*p*-F-$C_6H_4S]_4Sn$ 2. *p*-F-C_6H_4SH (1.85 ml, 17.4 mmol) was dissolved in dry toluene (60 ml) and $SnCl_4$ (0.5 ml, 4.28 mmol) added dropwise. Ammonia was slowly bubbled through the reaction mixture, causing a white precipitate of NH_4Cl. This bubbling was continued until no more precipitate was formed. The NH_4Cl was removed by filtration, and the toluene removed *in vacuo* to leave a white solid. Recrystallisation from ether gave **2** as colourless crystals (1.85 g, 69%; mp 54 °C).Analysis, found (calculated for $C_{24}H_{16}F_4S_4Sn$): C 45.0(45.9), H 2.6(2.6)%; ^1H NMR: 6.86 (2H, d, $J = 8.6$ Hz), 7.16 (2H, dd, $J = 8.8$, 5.3 Hz); ^{13}C NMR: 116.3 (d, $^2J_{C\text{-}F} = 22$ Hz, *m*-CH), 123.4 (*o*-CH), 162.9 (d, $^1J_{C\text{-}F} = 249$ Hz, CF); ^{19}F NMR: −113.2 (m, $J = 4.5$ Hz); ^{119}Sn NMR: 49.8 ppm.

$[CF_3CH_2S]_4Sn$ 3. Against a dry nitrogen counterflow CF_3CH_2SH (3.05 ml, 34.3 mmol) was syringed into a pre-cooled flask at −78 °C. Once the CF_3CH_2SH had fully solidified, $SnCl_4$ (1.0 mL, 8.55 mmol) was added *via* syringe and this too was allowed to freeze. When both reagents were fully solid, the cooling bath was removed and the flask was allowed to warm slowly to room temperature, with vigorous stirring. During this warming, and the subsequent stirring at room temperature (1 h) the flask was intermittently vented to allow egress of the nascent HCl gas. Once the production of HCl was complete (as judged using universal indicator paper) stirring was stopped leaving **3** (4.16 g, 84%) as a highly volatile (bp 35 °C), clear liquid (**stench**). ^1H NMR: 2.33 (br m, 8H, CH_2); ^{13}C NMR: 30.3 (q, $^2J_{C\text{-}F} = 34.9$ Hz, CF_3CH_2), 124.9 (q, $^1J_{C\text{-}F} = 276$ Hz, CF_3CH_2); ^{19}F NMR: −68.2 (t, $^3J_{H\text{-}F} = 9.2$ Hz, CF_3); ^{119}Sn NMR: −70.3 ppm; IR (neat liquid): 2963s 2926m 1260vs 1090vs,br 1019vs cm^{-1}.

Crystallography

A crystal of **1** of approximate dimensions 0.2 × 0.2 × 0.18 mm was used for data collection. Crystal data: $C_{32}H_{16}F_{52}S_4Sn$, $M = 1635.38$, monoclinic, $a = 46.295(5)$, $b = 5.334(1)$, $c = 20.156(2)$ Å, $\beta = 94.11(1)°$, $U = 4964.5(12)$ Å^3, space group *C*2/*c*, $Z = 4$, μ(Mo-Kα) = 0.910 mm^{-1}. Crystallographic measurements were made at 170(2) K on a CAD4 automatic four-circle diffractometer in the range $2.03 < \theta < 24.97°$. Data (4619 reflections) were corrected for Lorentz and polarization effects and also for extinction. In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant. The asymmetric unit of **1** corresponds to half of one whole molecule with the central tin atom located on a special position with 2-fold rotational site-symmetry. The solution of the structure (SHELX 86)[21] and refinement (SHELX 93)[22] converged to a conventional [*i.e.* based on 3482 F^2 data with $Fo > 4\sigma(Fo)$] $R1 = 0.0319$ and $wR2 = 0.0839$. Goodness of fit = 0.869. The max. and min. residual densities were 0.569 and −0.733 e Å^{-3} respectively. The asymmetric unit is shown in Fig. 1 along with the labelling scheme used. Selected metrical data are given in the caption.

CCDC 1145/248. See http://www.rsc.org/suppdata/jm/b0/b005863g/ for crystallographic files in .cif format.

Film deposition

Details of our CVD apparatus are given elsewhere.[15] APCVD reactions were carried out on a horizontal-bed cold-walled reactor. The substrate used was silica-coated glass supplied by Pilkington Glass plc, which was cleaned by wiping with petroleum spirit (bp 40–60 °C), washing with propan-2-ol and drying in air. The glass was placed on the horizontal graphite bed of the reactor which was heated with three Whatman cartridge heaters. Four independent gas lines were used in carrying out the reactions, each was heated to 60 °C under a minimal flow of nitrogen. The glass substrate was heated to a temperature between 300 and 600 °C. When the required temperatures were attained the reactor was left for a few minutes to reach thermal equilibrium. $(CF_3CH_2S)_4Sn$ (**3**) was admitted to the system *via* the use of a bubbler. Compound **3**, which boils at 35 °C, has sufficient volatility at room temperature such that no heating of the bubbler assembly was required to deliver the precursor to the substrate. Runs were carried out over 1 minute or 3 minute periods. Over 1 minute, films deposited were too thin to perform X-ray diffraction measurements, so reactions were repeated over 3 minutes. The flow rates through the lines were kept constant throughout the reactions and are detailed in Table 1. Nitrogen from the plain line flows over the glass during heating and cooling and is then diverted by way of a four-way valve up through the exhaust. Simultaneously, the nitrogen line through the bubbler is diverted into the reactor and carries the volatile precursor over the heated substrate. The turning of the four-way valve marked the beginning and end of the reaction time.

Results and discussion

Synthesis and crystallography

Three homoleptic tin derivatives of fluorinated thiols have been prepared as potential precursors for the APCVD of tin sulfides. Since the C–F bond is vulnerable to attack by metal cations, a

Table 1 Gas flow rates relating to experimental conditions

Line	Flow rate/dm^{3}min^{-1}
Bubbler line (N_2)	0.5
Bubbler diluent line (N_2)	10
Plain line (N_2)	10
N_2 diluent in H_2S line	1.5
H_2S	0.3

synthetic procedure was required which avoided the use of RSM (M = Li, Na). Compounds **1** and **2** were prepared from RSH and $SnCl_4$, dissolved in toluene, in the presence of base (NH_3).

$$4\ \mathrm{RSH} + \mathrm{SnCl_4} \xrightarrow[-\mathrm{NH_4Cl}]{\mathrm{NH_3/toluene}} (\mathrm{RS})_4\mathrm{Sn}$$

$$\mathrm{R} = \mathrm{CF_3(CF_2)_5CH_2CH_2}\ (\mathbf{1},\ 92\%),\ p\text{-}\mathrm{FC_6H_4}\ (\mathbf{2},\ 69\%)$$

Analysis of **1** indicated the presence of ammonia at a reproducible level over several preparations/recrystallisations and consistent with a formula **1**·1/2NH_3.

$(CF_3CH_2S)_4Sn$ **3**, which is highly volatile, could not be prepared by the above methodology as it could not be separated cleanly from the reaction solvent. Instead, the reagents were sequentially frozen into the reaction vessel at −78 °C then allowed to warm to room temperature with vigorous stirring to remove HCl. The resulting malodorous liquid (84%) gave a single resonance in the ^{119}Sn NMR (−70.3 ppm) indicating total conversion of the tin halide to the thiolate.

The Mössbauer data for **1** are noteworthy as they differ markedly from other $(RS)_4Sn$, which exhibit singlet spectra with chemical shifts *ca.* 1.4 mm s^{-1}. In contrast, the Mössbauer spectrum of **1** is a broad line ($\Gamma = 1.98$ mm s^{-1}) which fits best to a doublet (quadrupole splitting 0.74 mms^{-1}) and with an isomer shift 0.01 mm s^{-1}. It appears that the long fluorinated, thiolate substituents both deshield the tin and exaggerate the electronic asymmetry brought about by the non-tetrahedral geometry about tin (*see below*).

The structure of **1** has been determined as typical of the compounds prepared in this study and is shown in Fig. 1. It proved impossible to locate the NH_3 implied by the microanalysis, but this is perhaps unsurprising if it is hydrogen-bonded at random to the plethora of C–F functionalities and thus disordered over the lattice. The Sn–S distances [2.3817(9), 2.3960(9) Å] are similar to those in the only other structurally-authenticated, unfunctionalised homoleptic tin thiolate $(PhS)_4Sn$ [2.379(4), 2.401(4) Å],[18] and a similar spread of S–Sn–S angles are present [102.84(4)–113.17(3)°] as in $(PhS)_4Sn$ [106.0(1)–114.9(2)°] despite the perfectly symmetrical nature of the molecule. The long, fluorinated chains align in the lattice (Fig. 2) but there are no significant intermolecular interactions.

Deposition studies

The high volatility of **3** makes it the most attractive precursor of the three fluoroalkylthiolates prepared and detailed deposition studies have been performed on this species. No films were deposited in the absence of H_2S which is in contrast to the case for $(PhS)_4Sn$, where oxide films are deposited in the absence of this gas.[18] In both instances, however, H_2S promoted the formation of tin sulfides.

Deposition at $T < 400$ °C

Films deposited at temperatures up to and including 400 °C were yellow in colour and uniform across the entire surface of the substrate. The Raman spectrum of the film deposited at 400 °C (Fig. 3a) is dominated by the band at 314 cm^{-1} and corresponds to SnS_2.[23] The X-ray diffraction pattern of the film deposited over a period of 3 minutes is shown in Fig. 4a and shows preference for orientation in the (001) direction. The pattern was indexed using UnitCell and lattice parameters are $a = 3.641(3)$, $c = 5.93(2)$ Å, which compare well with literature values ($a = 3.62$–3.65, $c = 5.85$–5.90 Å).[12,13,24] EDAX (Energy Dispersive Analysis by X-rays) was carried out on all films discussed in this report though the glass substrate occupied much of the excitation volume. Tin and sulfur were observed in all films and, as expected, films deposited over a longer period were thicker. The tin : sulfur ratios of the films deposited over 1 minute are given in Table 2. These results demonstrate that the films deposited at 300 and 400 °C are slightly sulfur-deficient SnS_2. Collectively, the data confirm the deposition of tin(IV) sulfide at 400 °C. The SEM micrograph of the film (Fig. 5a) shows irregular, ovoid-shaped deposits with a wavy appearance similar to the film of SnS_2 deposited from $SnCl_4$/H_2S.[15]

Deposition at $400 < T < 500$ °C

Films deposited at 450 or 500 °C were brown with yellow tinges at the edges which is thought to be due to the cooler edges of

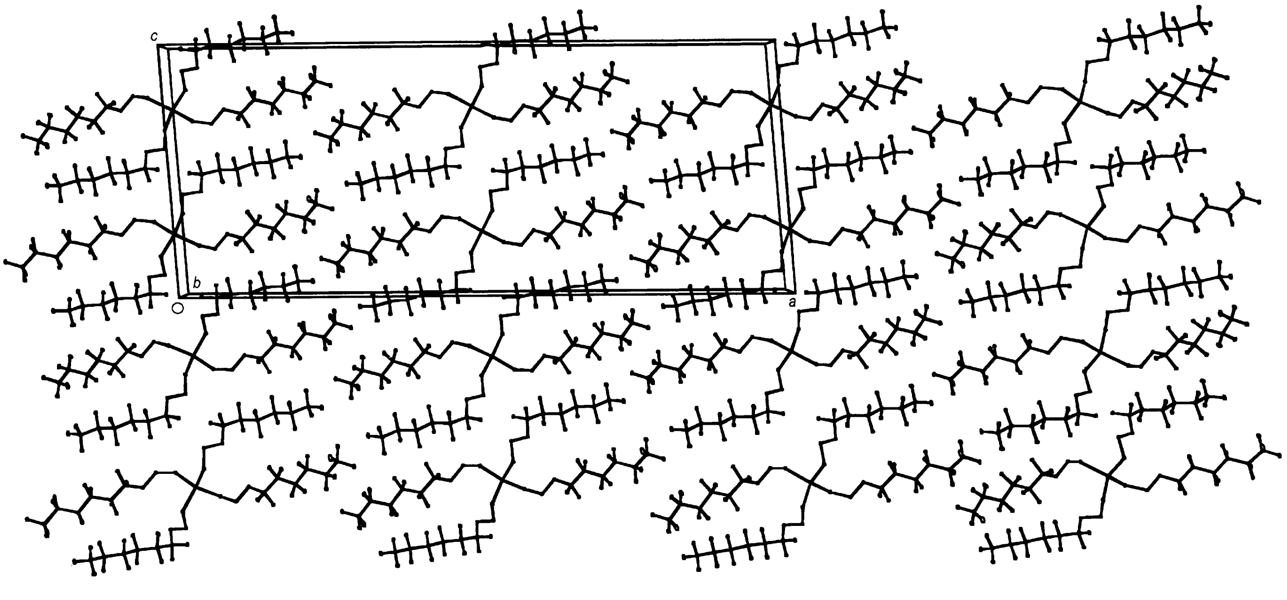

Fig. 2 The unit cell of **1** viewed perpendicular to the *ac* plane.

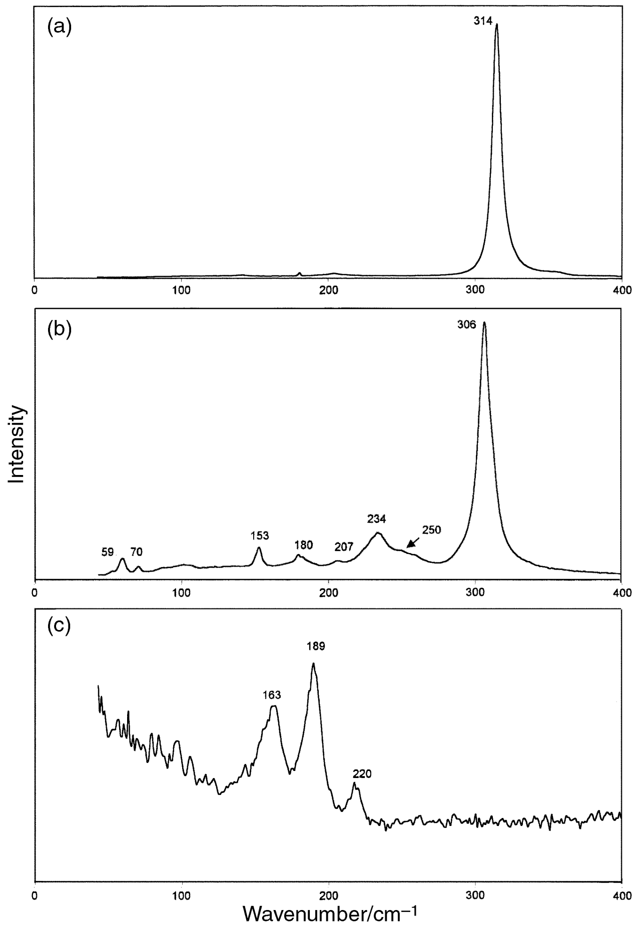

Fig. 3 Raman spectra of the films deposited at (a) 400, (b) 450 and (c) 600 °C.

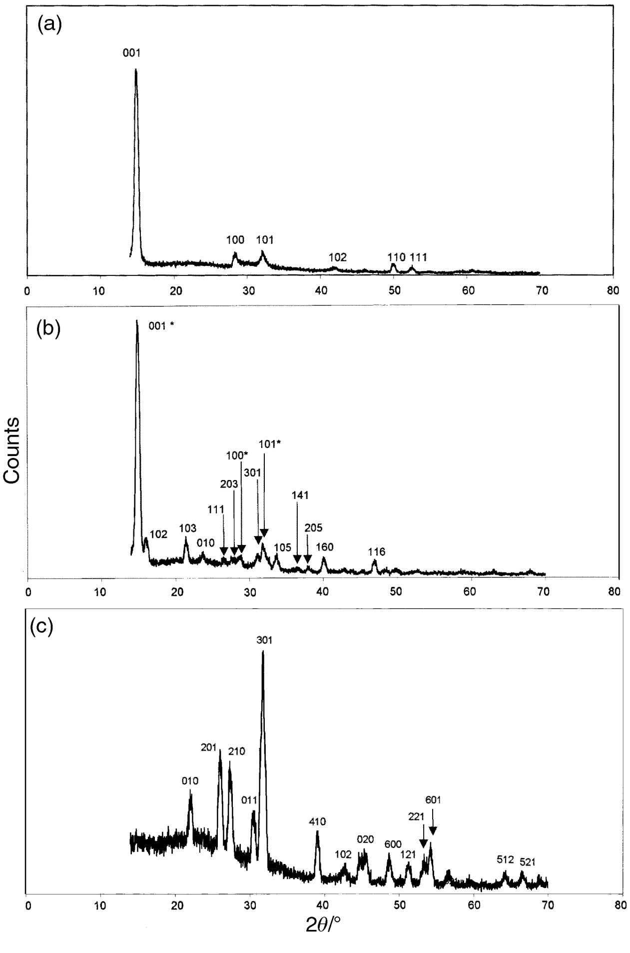

Fig. 4 XRD patterns produced by the films deposited at (a) 400, (b) 450 (peaks marked * are due to SnS_2) and (c) 600 °C.

the reactor bed. Fig. 3b shows the Raman spectrum of the film deposited at 450 °C and bands at 306, 250, 234, 180, 70, 59 cm^{-1} are consistent with this being Sn_2S_3.[25] Traces of SnS_2 are also evident (207 cm^{-1}; lit.[23] 209 cm^{-1}) but the absence of any band at 314 cm^{-1}, or even any appreciable broadening of the band at 306 cm^{-1}, suggest that the contamination is minor. The X-ray diffraction pattern of the film (Fig. 4b) generates lattice parameters [$a = 8.87(2)$, $b = 3.775(9)$, $c = 13.98(3)$ Å] which are comparable with literature values for Sn_2S_3 ($a = 8.80$–8.84, $b = 3.75$–3.77, $c = 14.02$ Å).[26,27] There is pronounced preferential growth in the (120) direction and the SEM micrograph shows the formation of needle-like growths (Fig. 5b). There is evidence for some contamination by SnS_2, notably the large peak at $2\theta = 14.9°$, but we have previously noted that SnS_2 is the dominant X-ray scatterer of the tin sulfide phases (see ref. 15 for comparative XRD spectra obtained under similar conditions; note the relative signal : -noise ratios). EDAX analysis of the film deposited at 450 °C has a Sn : S stoichiometry which is also consistent with deposition of a mixed-valence material (Table 2) though by 500 °C some loss of sulfur is evident. Any major SnS_2 contamination is also ruled out by this analysis.

Deposition at $T > 525$ °C

Films deposited at temperatures in excess of 525 °C were grey in appearance. The Raman spectrum of the film (Fig. 3c) deposited at 600 °C shows bands at 220, 189 and 163 cm^{-1} which compares well with those reported previously for SnS crystals with random orientation.[28] The XRD pattern produced by the film deposited at 600 °C is shown in Fig. 4c. Derived lattice parameters [$a = 11.227(19)$, $b = 3.978(5)$, $c = 4.246(7)$ Å] compare favourably with known data for SnS ($a = 11.18$–11.21, $b = 3.98$–4.02, $c = 4.30$–4.33 Å).[12,29–32] EDAX analyses of the films deposited at 550 and 600 °C are also consistent with the deposition of SnS, with a slight deficiency of sulfur (Table 2). SEM micrographs show that needle-like deposits formed at 550 °C (Fig. 5c) give way to block-shaped crystallites at 600 °C (Fig. 5d).

X-Ray photoelectron spectra have been recorded on all the films and the reported binding energies (*below*) are recorded from the bulk of the sample after Ar^+ etching. The Sn $3d_{5/2}$ binding energies observed in the films deposited at 300 and 550 °C are 486.0 and 485.5 eV respectively. SnS has a tin binding energy of 485.6 eV.[33] In direct comparison with the oxides, it is to be expected that tin(IV) sulfide would have a lower tin binding energy than tin(II) sulfide by 0.3 eV, but it is seen here that the binding energy of tin in the film deposited at 300 °C is 0.5 eV higher. The S 2p binding energies in the films deposited at 300 and 550 °C are 161.3 and 161.1 eV, respectively. The binding energy of sulfur in the related ZnS is reported in the literature as being 161.7 eV.[33] As sulfur binding energies vary to a much greater degree than tin binding energies it is clear that this is indicative of sulfur in a metal environment.

Table 2 Film stoichiometry determined by EDAX

Deposition temperature/°C	Sn : S ratio
300	1 : 1.80
400	1 : 1.88
450	1 : 1.52
500	1 : 1.38
550	1 : 0.96
600	1 : 0.95

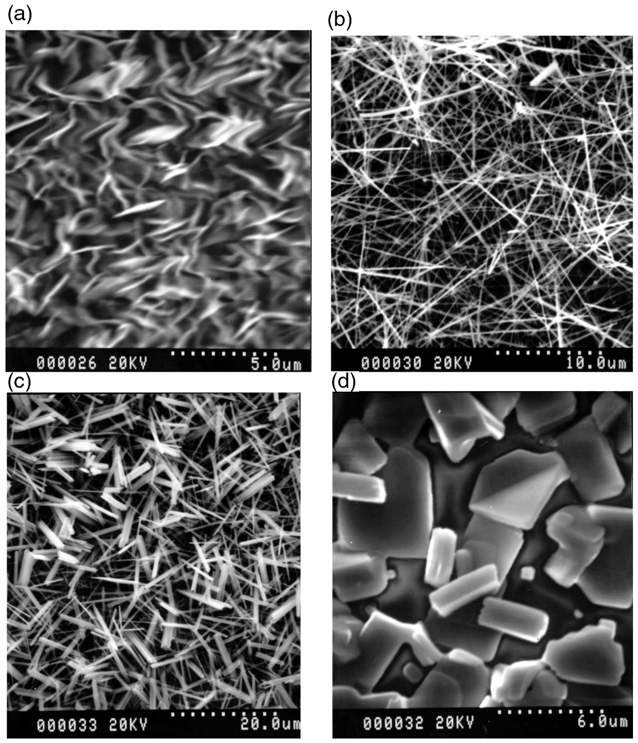

Fig. 5 SEMs of the films deposited at (a) 400, (b) 450, (c) 550 and (d) 600 °C.

It is notable that in the deposition experiments described herein which use **3** as precursor, greater temperature control over film stoichiometry has been achieved than we have previously reported using $(PhS)_4Sn$,[18] where only mixed-phase films were evident.

Conclusions

Highly volatile tin(IV) thiolates, which can be generated by the incorporation of fluoroalkyl substituents on sulfur, afford the first instance of APCVD of tin sulfide films from a Sn–S precursor. H_2S is, however, required as co-reagent for film formation. The Raman, X-ray diffraction, EDAX and XPS all concur that films deposited at 300 and 400 °C are composed of sulfur-deficient tin(IV) sulfide, films deposited at 450 and 500 °C comprise the sesquisulfide, Sn_2S_3, and the films deposited at 550 or 600 °C are sulfur-deficient tin monosulfide, SnS. $(CF_3CH_2S)_4Sn$ affords better temperature-controlled phase selectivity in the deposited films than when using $(PhS)_4Sn$ as precursor in AACVD experiments.

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