CHEMISTRY OF MATERIALS

Organotin Dithiocarbamates: Single-Source Precursors for Tin Sulfide Thin Films by Aerosol-Assisted Chemical Vapor Deposition (AACVD)

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Supporting Information

ABSTRACT: A series of diorganotin complexes of dithiocarbamates $[Sn(C_4H_9)_2(S_2CN(RR')_2)_2]$ (R, R' = ethyl (1); R = methyl, R' = butyl (2); R, R' = butyl (3); R = methyl, R' = hexyl (4); and $[Sn(C_6H_5)_2(S_2CN(RR')_2)_2]$ (R, R' = ethyl (5); R = methyl, R' = butyl (6); R, R' = butyl (7); R = methyl, R' = hexyl (8) were synthesized. Single-crystal X-ray structures of 2, 3, and 8 were determined. Thermogravimetric analysis (TGA) showed single-step decomposition for the complexes 1, 3, and 5–8, and double-step decomposition for the complexes 2 and



4 between 195 °C and 325 °C. Complexes 1–4 were used as single-source precursors for the deposition of SnS thin films by aerosol-assisted chemical vapor deposition (AACVD) at temperatures from 400 °C to 530 °C. Orthorhombic SnS thin films were deposited from all four complexes at all deposition temperatures. The films were characterized by UV–vis spectroscopy, powder X-ray diffraction (p-XRD), Raman spectroscopy, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and also electrical resistivity measurements.

KEYWORDS: diorganotin dithiocarbamate, single source precursors, tin sulfide, thin films, aerosol-assisted chemical vapor deposition

INTRODUCTION

Tin sulfide is a IV–VI semiconductor and exists in three main forms, including SnS, SnS₂, and Sn₂S₃.¹ It has attracted particular attention as a low-toxicity solar energy absorber,^{2,3} in holographic recording,^{4,5} and for infrared detection.⁶ The band gaps of SnS, SnS₂, and Sn₂S₃ are 1.3 eV, 2.18 eV, and 0.95 eV, respectively.^{7–9} All three forms of tin sulfides exhibit semiconducting properties; however, SnS has attracted the most attention, because of its electronic bandgap, which lies midway between those of elemental silicon and GaAs.⁹ It has been reported that, depending on the tin content, SnS may be a *p*-type or *n*-type conductor and may also change its conductivity upon heat treatment.¹⁰ SnS₂ is an *n*-type semiconductor, and Sn₂S₃ has highly anisotropic conduction.¹⁰

Many methods have been used to prepare tin sulfide thin films, including spray pyrolysis,¹¹ dip deposition,¹² chemical vapor deposition,^{13–16} thermal evaporation,¹⁷ chemical bath deposition,²² and melt growth.²³ In addition, a variety of methods have been employed to prepare tin sulfide nanostructures, including hydrothermal methods,²⁴ solvothermal methods,²⁵ the hot injection method,²⁶ the aqueous solution method,²⁷ and polyol methods.^{28,29}

Chemical vapor deposition (CVD) methods have the attraction of being able to deposit relatively large area films at

higher growth rate. In particular, CVD using single-source precursors possess some potential intrinsic advantages, such as improved air/moisture stability of the precursor, excluding prereactions and lower toxicity.³⁰ Accordingly, various singlesource precursors for the deposition of tin sulfide thin films have been investigated recently; examples include thiolates ${Sn(SCH_2CF_3)_4, Sn(SPh)_4, and Sn(SCy)_4}^{13,31}$ dithiolates ${Sn(SCH_2CH_2S)_2}$,³² dithiocarbamates ${Sn(S_2CNEt_2)_4}$,³³ and organotin unsymmetrical dithiocarbamates, {R_nSn[S₂CN- $(C_4H_9)CH_3]_{4-n}$, where R = Me, Bu, or Ph and $n = 1, 2, \text{ or } 3.^{34}$ However, all these precursors require H₂S as a sulfur source to deposit tin sulfide.³² This behavior was attributed to a facile disulfide (RS-SR) elimination pathway. Subsequent molecular orbital calculations and an extensive literature search revealed that the general class of $[M(SR)_4]$ molecules (where M is a Group IV element) suffer significant distortions from tetrahedral geometry, because of noncovalently bonded S…S interactions.²⁹ This distortion and *cis*-annular interaction promotes this disulfide elimination pathway. Recently, we have studied the deposition behavior of tribenzyltin chloridethiosemicarbazone compounds by aerosol-assisted chemical

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Table 1. Crystallinity Data for Compounds 2, 3, and 8^a

parameter	2	3	8
formula	$C_{20}H_{42}N_2S_4Sn$	$C_{52}H_{102}N_4S_8Sn_2$	$C_{28}H_{42}N_2S_4Sn$
formula weight, M	557.49	1277.24	653.63
appearance	colorless plates	colorless block	colorless block
system and space group	monoclinic, C2/c	monoclinic, $P2_1/n$	monoclinic, C2/c
unit-cell dimensions			
а	21.936(3) Å	20.345(5) Å	27.282(9) Å
b	7.164(1) Å	9.597(5) Å	17.766(6) Å
с	21.873(2) Å	34.350(5) Å	18.671(6) Å
β	127.45°	91.27°	96.77°
V	2728.8(6) Å ³	6705(4) Å ³	8987.3(5) Å ³
Ζ	4	4	12
density, D	1.357 Mg/m ³	1.265 Mg/m ³	1.449 Mg/m ³
emperature, T	180(2) K	100(2) K	100(2) K
reflections collected/unique reflections	8178/3198	28488/14787	6019/4943
R _{int}	0.0626	0.0286	0.0297
for $[I > 2\sigma(I)]$			
R_1	0.0378	0.0318	0.0339
wR_2	0.0601	0.0927	0.0821
for all data			
R_1	0.0715	0.0482	0.0447
wR_2	0.0647	0.0755	0.0857
argest diff. peak and hole	0.555 and $-0.610 \text{ e } \text{A}^{-3}$	1.533 and -1.168 e A ⁻³	1.644 and -0.607 e A^{-3}
goodness of fit, GOF	0.763	1.016	1.054

^{*a*}CCDC Nos. 806740 (for 2), 806738 (for 3), and 806739 (for 8) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

vapor deposition (AACVD).¹⁶ In the search for new singlesource precursors to deposit high-quality tin sulfide thin films without the use of H_2S , here, we report the synthesis and characterization of symmetric and unsymmetric diorganotin dithiocarbamates. Single-crystal X-ray structures of tin complexes 2, 3, and 8 were determined. Complexes 1–4 were used as single-source precursors for the deposition of tin sulfide thin films by AACVD. Parkin et al. demonstrated that the unsymmetric organotin dithiocarbamates could deposit tin sulfide films by APCVD with H_2S gas.³⁴ Therefore, our interest is in the development of symmetric and unsymmetric diorganotin dithiocarbamates as precursors for the deposition of tin sulfide thin films by AACVD without any external sulfur source or co-reagent.

EXPERIMENTAL SECTION

Author: All preparations were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques. All reagents were purchased from Sigma-Aldrich Chemical Company and used as received. Solvents were distilled prior to use. Mass spectra were recorded on a Kratos Concept 1S instrument. Infrared spectra were recorded on a Specac single-reflectance attenuated total reflectance (ATR) instrument (4000–400 cm⁻¹, resolution of 4 cm⁻¹). Elemental analysis was performed by the microanalytical laboratory at the University of Manchester. ¹H and ¹¹⁹Sn NMR spectra were recorded in CDCl₃ solution (unless specified) on a Bruker spectrometer operating at 400.0 MHz. The chemical shifts are referenced with respect to tetramethylsilane (for ¹H) and tetramethyltin (for ¹¹⁹Sn). All the ¹¹⁹Sn NMR spectra were recorded under broadband decoupled conditions. TGA measurements were carried out by a Seiko SSC/S200 model under a heating rate of 10 °C min⁻¹ under nitrogen. The electrical conductivity and Hall coefficient were measured in the temperature range of 77-340 K by the van der Pauw technique using an Ecopia Hall Measurement System (HMS-3000) with a custom-built cryogenic cooling system and a 0.55 T magnet. Soldered indium

electrodes were used for the fabrication of the ohmic contacts. Raman spectra were recorded using a Perkin–Elmer Model 400F Raman spectrometer.

X-ray Crystallography. Single-crystal X-ray diffraction (XRD) data for the compounds were collected using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) on a Bruker APEX diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares³⁵ on F². All non-H atoms were refined anisotropically. H atoms were included in calculated positions, assigned isotropic thermal parameters, and allowed to ride on their parent C atoms. All calculations were carried out using the SHELXTL package.³⁶ The details pertaining the data collection of the crystals are given in Table 1.

Deposition of Films by AACVD. In a typical deposition, 0.20 g of the precursor was dissolved in 10 mL of toluene in a two-necked 100 mL round-bottom flask with a gas inlet that allowed the carrier gas (argon) to pass into the solution to aid the transport of the aerosol. This flask was connected to the reactor tube by a piece of reinforced tubing. The argon flow rate was controlled by a Platon flow gauge. Seven borosilicate glass substrates (\sim 1 cm \times 3 cm and 1 mm thick) were placed inside the reactor tube, which is placed in a Carbolite furnace. The precursor solution in a round-bottom flask was kept in a water bath above the piezoelectric modulator of a PIFCO ultrasonic humidifier (Model No. 1077). The aerosol droplets of the precursor thus generated were transferred into the hot wall zone of the reactor by carrier gas. Both the solvent and the precursor were evaporated and the precursor vapor reached the heated substrate surface, where thermally induced reactions and film deposition occurred.

Characterization of Thin Films. XRD studies were performed on a Bruker AXS D8 diffractometer, using Cu K α radiation. The samples were mounted flat and scanned over a range of 20°–80° in a step size of 0.05° with a count rate of 9 s. Films were carbon-coated using an Edwards Model E306A coating system before carrying out SEM and EDX analyses. SEM analysis was performed using a Philips XL 30FEG system, and EDX was carried out using a DX4 instrument.

Synthesis of $[Sn(C_4H_9)_2(S_2CN(C_2H_5)_2)_2]$ (1). Complex 1 was synthesized by a literature method,³⁷ sodium *N*,*N*-diethyldithiocarba-

Scheme 1. Synthesis of Compounds 1-8



mate (3.0 g, 1.3 mmol) and di-*n*-butyltin dichloride (2.02 g, 0.65 mmol) were dissolved in ethanol (200 mL) and stirred for 30 min, during which time a fine sodium chloride powder precipitated. The reaction mixture was filtered and the ethanol removed from the filtrate by vacuum distillation. The resulting white solid was recrystallized from ethanol chloroform (1:1) to give colorless crystalline plates. Yield = 4.2 g (60.0%). Mp: 57 °C. IR (ν_{max}/cm^{-1}): 2953(w), 2924(w), 1483(s), 1456(m), 1417(s), 1353(m), 1298(m), 1253(s), 1205(s), and 1138(s). Elemental analysis: Calc. for C₁₈H₃₈N₂S₄Sn: C, 40.8; H, 7.2; N, 5.3; S, 24.2; Sn, 22.4%. Found: C, 39.9; H, 7.5; N, 5.1; S, 22.8; Sn, 21.4%. ¹H NMR (δ /ppm): 0.86 (6H, t, *J* = 8, Bu CH₃), 1.22 (12H, t, *J* = 8, CH₃), 1.37 (4H, m, Bu CH₂), 1.85 (4H, m, Bu CH₂), 1.99 (4H, m, Bu CH₂), 3.80 (8H, q, NCH₂); ¹¹⁹Sn NMR (δ /ppm): -336.2(s).

Synthesis of [Sn(C₄H₉)₂(S₂CN(CH₃)(C₄H₉))₂] (2). Complex 2 was synthesized by dissolving sodium hydroxide (2.3 g, 5.7 mmol), methylbutylamine (5.0 g, 5.7 mmol) in ethanol (100 mL) and stirring for 30 min, followed by the addition of CS₂ (3.47 mL, 5.7 mmol) and stirring for 1 h. A solution of di-n-butyltin dichloride (8.7 g, 2.85 mmol) in ethanol (25 mL) was added dropwise and stirred for 30 min, during which time fine sodium chloride powder precipitated. The reaction mixture was filtered and the solvent was evaporated from the filtrate by vacuum distillation to leave an oily product. Colorless blocks of crystals were formed after leaving the resulting product in a refrigerator after a month. Yield = 8.2 g (51.5%). Mp: 41 °C. IR (v_{max} / cm^{-1}): 2954(w), 2922(w), 2868(w), 1485(s), 1462(m), 1431(m), 1389(s), 1293(m), 1248(m), 1204(s), and 1138(s). Elemental analysis: Calc. for $C_{20}H_{42}N_2S_4Sn$: C, 43.1; H, 7.6; N, 5.0; S, 23.0; Sn, 21.3%. Found: C, 43.3; H, 8.6; N, 4.9; S, 21.7; Sn, 21.5%. ¹H NMR (δ/ppm) : 0.86 (6H, t, J = 7.2, Bu CH₃), 1.17 (6H, t, J = 7.2, Bu CH₃), 1.29 (4H, m, CH₂), 1.35 (4H, m, CH₂), 1.63 (4H, m, CH₂), 1.84 (4H, m, CH₂), 1.97 (4H, m, CH₂), 3.32 (6H, s, NCH₃), 3.78 (4H, t, J = 8, NCH₂); ¹¹⁹Sn NMR (δ /ppm): -339.5(s).

Synthesis of $[Sn(C_4H_9)_2(S_2CN(C_4H_9)_2)_2]$ (3). Complex 3 was synthesized by following the method given for complex 2, but using di*n*-butylamine (7.3 g, 5.7 mmol) as the amine source. White solid, yield = 7.4 g (40.2%). Mp: 50 °C, IR (ν_{max}/cm^{-1}): 2955(w), 2929(w), 2869(w), 1493(s), 1426(m), 1391(w), 1296(m), 1221(m), and 1148(s), Elemental analysis: Calc. for C₂₆H₅₄N₂S₄Sn: C, 48.7; H, 8.5; N, 4.4; S, 20.0; Sn, 18.5%. Found: C, 48.6; H, 9.3; N, 4.3; S, 18.8; Sn, 18.8%. ¹H NMR (δ/ppm): 0.86 (6H, t, *J* = 8, Bu CH₃), 0.88 (12H, t, *J* = 8, Bu CH₃), 1.28 (8H, m, CH₂), 1.35 (4H, m, CH₂), 1.63 (8H, m, CH₂), 1.84 (4H, m, CH₂), 1.97 (4H, m, CH₂), 3.71 (8H, t, *J* = 8, NCH₃); ¹¹⁹Sn NMR (δ/ppm): -338.4(s).

Synthesis of [Sn(C_4H_9)_2(S_2CN(CH_3)(C_6H_{13}))_2] (4). Complex 4 was synthesized by following the method given for complex 2, but using methylhexylamine (6.5 g, 5.7 mmol) as the amine source. Colorless oil, yield = 7.8 g (44.3%). IR (v_{max}/cm^{-1}): 2953(w), 2926(w), 2865(w), 1489(s), 1467(m), 1441(m), 1395(s), 1299(m), 1253(m), and 1204(s). Elemental analysis: Calc. for $C_{24}H_{50}N_2S_4Sn: C$, 46.9; H, 8.2; N, 4.6; S, 21.0; Sn, 19.4%. Found: C, 47.4; H, 8.8; N, 4.5; S, 19.5; Sn, 19.1%. ¹H NMR (δ/ppm): 0.65 (6H, t, *J* = 8, Hex CH₃), 1.05 (6H, t, *J* = 8, Bu CH₃), 3.13 (6H, t, *J* = 8, NCH₂) 3.58 (4H, t, *J* = 8, NCH₃); ¹¹⁹Sn NMR (δ/ppm): -340.4(s).

Synthesis of [Sn(C₆H₅)₂(S₂CN(C₂H₅)₂)₂] (5). Complex 5 was synthesized by following the method given for complex 1, but using diphenyltin dichloride (4.4 g, 0.65 mmol) as the tin source. White solid, yield = 5.4 g (74%). Mp: 150 °C. IR (v_{max} /cm⁻¹): 2956(w), 2923(w), 2868(w), 1493(s), 1426(s), 1369(w), 1297(w), 1221(m), 1148(m), and 985(w). Elemental analysis: Calc. for C₂₂H₃₀N₂S₄Sn: C, 46.4; H, 5.3; N, 4.9; S, 22.5; Sn, 20.8%. Found: C, 46.4; H, 5.5; N, 4.9; S, 22.4; Sn, 20.9%. ¹H NMR (δ/ppm): 1.19 (12H, q, CH₃), 3.69 (8H, t, *J* = 8, NCH₂), 7.27 (SH, m, ArH) 7.76 (SH, m, ArH); ¹¹⁹Sn NMR (δ/ppm): -501.5(s).

Synthesis of $[Sn(C_6H_5)_2(S_2CN(CH_3)(C_4H_9))_2]$ (6). Complex 6 was synthesized by following the method given for complex 2, but using diphenyltin dichloride (9.7 g, 2.85 mmol) as the tin source. White solid, yield = 6.7 g (39.7%). Mp: 133 °C. IR (v_{max}/cm^{-1}): 2955(w), 2924(w), 1485(s), 1418(m), 1354(w), 1264(s), 1207(m), 1139(m), 1073(m), and 995(w). Elemental analysis: Calc. for C₂₄H₃₄N₂S₄Sn: C, 48.2; H, 5.7; N, 4.7; S, 21.5; Sn, 19.9%. Found: C, 48.3; H, 5.9; N, 4.6; S, 21.2; Sn, 20.2%. ¹H NMR (δ /ppm): 0.99 (6H, t, *J* = 8, Bu CH₃), 1.39 (4H, m, Bu CH₂), 1.73 (4H, m, Bu CH₂), 3.36 (6H, s, NCH₃),



Figure 1. Molecular structures of (a) **2**, (b) **3**, and (c) **8** are shown with 50% ellipsoidal probability level. All the H atoms on carbon frames are removed for clarity. Selected bond lengths (Å) and bond angles (°) for **2**: Sn1–S1, 2.526(1); Sn1–S2, 2.940(1); Sn1–C7, 2.130(3); S1–C1, 1.736(3); S2–C1, 1.697(4); and C7–Sn1–C7*, 137.63(2); S1–Sn1–S1*, 83.93(5); S2–Sn1–S2*, 145.68(3); S2–C1–S1, 119.6(2). Selected bond lengths (Å) and bond angles (°) for **3**: Sn1–S1, 2.507(1); Sn1–S2, 2.894(1); Sn1–S3, 2.524(1); Sn1–S4, 3.029(1); Sn1–C19, 2.152(3); Sn1–C23, 2.133(3); S1–C1, 1.754(3); S2–C1, 1.698(3); S3–C10, 1.740(3); S4–C10, 1.690(3); and C19–Sn1–C23, 129.13(1); S1–Sn1–S3, 82.23(3); S2–Sn1–S4, 147.85(3); S2–C1–S1, 119.15(2); S3–C10–S4, 119.79(2); for **8**: Sn1–S1, 2.498(1); Sn1–S2, 2.983(1), Sn1–S3, 2.505(1); Sn1–S4, 2.933(1); Sn1–C17, 2.128(3); Sn1–C23, 2.135(3); S1–C1, 1.745(4); S2–C1, 1.692(4); S3–C9, 1.741(4); S4–C9, 1.699(4); and C17–Sn1–C23, 136.89(15); S1–Sn1–S3, 83.87(3); S2–Sn1–S4, 145.30(3); S2–C1–S1, 120.1(2); S3–C9–S4, 119.5(2).

3.78 (4H, t, J = 8, NCH₂), 7.41 (5H, m, ArH), 7.93 (5H, m, ArH); ¹¹⁹Sn NMR (δ /ppm): -505.8(s).

Synthesis of [Sn(C₆H₅)₂(S₂CN(C₄H₉)₂)₂] (7). Complex 7 was synthesized by following the method given for complex 2, but using di*n*-butylamine (7.3 g, 5.7 mmol) as the amine source and diphenyltin dichloride (9.7 g, 2.85 mmol) as the tin source. White solid, yield = 8.2 g (56.6%). Mp: 97 °C. IR (ν_{max}/cm^{-1}): 2955(w), 2929(w), 1492(s), 1426(m), 1369(w), 1298(m), 1262(m), and 1220(m). Elemental analysis: Calc. for C₃₀H₄₆N₂S₄Sn: C, 52.9; H, 6.9; N, 4.1; S, 18.8; Sn, 17.4%. Found: C, 52.9; H, 7.3; N, 4.1; S, 18.4; Sn, 17.5%. ¹H NMR (*δ*/ppm): 0.99 (12H, t, *J* = 8, Bu CH₃), 1.39 (8H, m, Bu CH₂), 1.78 (8H, m, Bu CH₂), 3.75 (8H, t, *J* = 8, NCH₂), 7.41 (5H, m, ArH), 7.92 (SH, m, ArH); ¹¹⁹Sn NMR (*δ*/ppm): -506.3(s).

Synthesis of [Sn(C_6H_5)_2(5_2CN(CH_3)(C_6H_{13}))_2] (8). Complex 8 was synthesized by following the method given for complex 2, but using methylhexylamine (6.5 g, 5.7 mmol) as the amine source and diphenyltin dichloride (9.7 g, 2.85 mmol) as the tin source. White solid, yield = 5.8 g (47%). Mp: 120 °C. IR (v_{max}/cm^{-1}): 2956(w), 2928(w), 1492(s), 1426(s), 1390(w), 1297(m), 1261(m), and

1221(m). Elemental analysis: Calc. for $C_{28}H_{42}N_2S_4Sn: C, 51.5; H, 6.5; N, 4.3; S, 19.6; Sn, 18.2%. Found: C, 51.9; H, 6.7; N, 4.3; S, 19.0; Sn, 18.2%. ¹H NMR (<math>\delta$ /ppm): 0.96 (6H, t, *J* = 8, Hex CH₃), 1.37 (8H, m, Hex CH₂), 1.75 (4H, m, Hex CH₂), 3.36 (6H, s, NCH₃), 3.78 (4H, t, *J* = 8, NCH₂), 7.41 (5H, m, ArH), 7.95 (5H, m, ArH); ¹¹⁹Sn NMR (δ /ppm): -506.8(s).

RESULTS AND DISCUSSION

Synthesis. Two synthetic procedures have been employed for the synthesis of diorganotin dithiocarbamate complexes. The first method involves the reaction of a diorganotin dichloride, R_2SnCl_2 (R = *n*-Bu or Ph) with sodium *N*,*N*diethyldithiocarbamate in a 1:2 stoichiometric ratio in ethanol to give mononuclear complexes 1 and 5 in quantitative yields (see Scheme 1). The second method involves the in situ synthesis of dithiocarbamates and then reaction with diorganotin dichloride, R_2SnCl_2 (R = *n*-Bu or Ph) in a stoichiometric ratio of 2:1. It also produces mononuclear complexes 2-4 and 6-8 in quantitative yields (see Scheme 1).

Complexes 2 and 4 are colorless viscous oils, whereas the other complexes are white solids; all of them are soluble in all common organic solvents. We were able to crystallize complex 2 from viscous oil after leaving it refrigerated at 5 °C for a month. Compounds 1–8 show a single resonance in their ¹¹⁹Sn NMR spectra in a narrow chemical shift window ranging from –336.0 ppm to –340.0 ppm for compounds 1–4 (di-*n*-butyltin derivatives) and –501.0 ppm to –506.0 ppm for compounds 5–8 (diphenyltin derivatives), indicating the presence of only one type of Sn atom in the structure. These chemical shifts are the signature of diorganotin dithiocarbamate complexes that contain a single Sn atom with a 2C, 2S coordination environment in solution.^{38–40}

Single-Crystal X-ray Structures of 2, 3, and 8. Complexes 2, 3, and 8 also have been characterized by single-crystal X-ray analysis. Their molecular structures and selected bonding parameters are given in Figure 1. The structure determination for 2 was difficult; at low temperatures, crystals cracked, possibly because of a phase change, and final data were collected at 180 K on a relatively small crystal. Application of absorption corrections did not improve the refinement, and the thermal ellipsoids on the alkyl substituents are quite large. Despite attempts, no better solutions were found. The molecular structures of all three compounds are isostructural, but each has different substituents, either on tin or in the dithiocarbamate moiety. The structure of 2 is discussed here as an example. The structure determination reveals that the diorganotin bis(dithiocarbamate) adopts a well-known discrete structure.^{38–40} The asymmetric unit of 2 contains half of the molecule, with one Sn atom (Sn1) sitting on a special position along a 2-fold axis. The tin is involved in four covalent bonds (2C and 2S), having a distorted tetrahedral geometry.

The other S atom on each dithiocarbamate moiety (S2 and S2*) is involved in a weaker bonding interaction with tin along the tetrahedral faces (Figure 1a). Accordingly, two types of Sn-S distances are seen. The comparatively shorter Sn1–S1 and Sn1–S1* (2.526(1) Å) distances correspond to Sn–S covalent bonds; whereas, the Sn1–S2 and Sn1–S2* (2.940(1) Å) distances correspond to the Sn–S weaker bonding. The sum of the van der Waals radii of tin and sulfur is 3.97 Å.⁴¹ In view of this and also in view of literature precedents,^{38–40} it can be concluded that a coordinative interaction exists between Sn1 and S1 and S2, with each dithiocarbamate moiety shown chelating an isobidentate coordination mode. Consequently, the Sn atom is six-coordinated with a 2C, 4S coordination environment, and the geometry around the Sn atom can be described as a skewed trapezoidal bipyramid (see Figure 1a).⁴²

Thermogravimetric analysis (TGA). Thermogravimetric analysis gives information about the decomposition and/or volatility of the complexes. TGA (25–500 °C; heating rate of 10 °C min⁻¹ under nitrogen) of the tin complexes (1 and 3) showed close to single-step decomposition, with weight loss occurring between 212 °C and 298 °C and between 214 °C and 294 °C, respectively (see Figure 2). The solid residue for 1 (27.8%) is in good agreement with calculated value of 28.4% for SnS. Similarly, for 3, the final residue (20.4%) is close to that which is expected for SnS (23.4%). Complex 2 decomposes in two steps between 198 °C and 274 °C, finally leading to 36.1%, which corresponds to the calculated value (37.1%) for SnS₂. The solid undergoes a second decomposition between 274 °C and 329 °C, with a total residue weight of Article



Figure 2. TGA of $[Sn(C_4H_9)_2(S_2CN(C_2H_5)_2)_2]$ (1) (black squares, \Box), $[Sn(C_4H_9)_2(S_2CN(CH_3)(C_4H_9))_2]$ (2) (red circles, \bigcirc), $[Sn(C_4H_9)_2(S_2CN(C_4H_9)_2)_2]$ (3) (blue triangles, \triangle), and $[Sn(C_4H_9)_2(S_2CN(CH_3)(C_6H_{13}))_2]$ (4) (golden orange diamonds, \diamondsuit) under a N₂ atmosphere.

8.9%. Complex 4 decomposes in two steps; the first step, between 220 °C and 303 °C, gives 30.2%, which is in good agreement with the value for SnS₂ (29.7%). The residue further decomposed at temperatures between 303 °C and 325 °C, with a residue weight of 19.0%. Further decomposition of SnS₂ has previously been noted and, in these cases, could be associated with oxygen leakage into the reactor.

Figure 3 shows a TGA graph of the diphenyl derivative of tin complexes. Complexes 5, 6, 7, and 8 showed single-step



Figure 3. TGA of $[Sn(C_6H_5)_2(S_2CN(C_2H_5)_2)_2]$ (5) (black squares, \Box), $[Sn(C_6H_5)_2(S_2CN(CH_3)(C_4H_9))_2]$ (6) (red circles, \bigcirc), $[Sn(C_6H_5)_2(S_2CN(C_4H_9)_2)_2]$ (7) (blue triangles, \triangle), and $[Sn(C_6H_5)_2(S_2CN(CH_3)(C_6H_{13}))_2]$ (8) (golden orange diamonds, \diamondsuit) under a N₂ atmosphere.

decomposition with weight loss occurring within the ranges of 242–300 °C, 242–318 °C, 247–321 °C, and 247–327 °C, respectively. The residue amounts of 26.5% for **5** agree well with the calculated value of 26.4% for SnS, and those for **6** (25.2%), 7 (20.1%), and **8** (21.5%) show agreement with the calculated values for SnS (25.1%, 22.0%, and 23.0%, respectively). We presume that these complexes follow nearly the same decomposition pathway as that reported for similar dithiocarbamate complexes.^{43,44}

Tin Sulfide Thin Films from Dibutyltin Dithiocarbamate Complexes. Thin films of tin sulfides were deposited on glass substrates using toluene solution of precursors 1-4 by

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AACVD. The film deposition temperature was varied over a range of 400–530 °C at an argon flow rate of 140 sccm. Substrate temperatures below 400 °C were not enough to initiate deposition. Using precursor 1 at 400 °C, a dense, brownish yellow adherent film was deposited, whereas at 450 and 500 °C, dark black films were deposited. Precursor 2 deposited dark brownish films at 400–500 °C and black adherent films were deposited at 530 °C. Precursor 3 deposited black adherent uniform films at all temperatures, whereas precursor 4 deposited brownish films at 400 and 450 °C and black films at 500 °C.

The XRD pattern of films deposited on a glass substrate at temperatures of 400-500 °C from a toluene solution of precursor 1 is shown in Figure 4. The diffraction peaks could be



Figure 4. XRD pattern of SnS films deposited from [Sn- $(C_4H_9)_2(S_2CN(C_2H_5)_2)_2$] (1) on a glass substrate: (a) 400 °C, (b) 450 °C, and (c) 500 °C. The asterisk symbol (*) denotes the SnO₂ phase.

indexed to the orthorhombic herzenbergite-SnS (ICDD File Card No. 033-1375). The relative highest intensity peak was observed at $2\theta = 31.49^{\circ}$, corresponding to the (111) plane of orthorhombic SnS. The major diffraction peaks could be indexed as the (120), (021), (101), (131), and (141) reflections of SnS. The relatively lower intensity peak at $2\theta = 33.50^{\circ}$ was observed, which could be indexed as a SnO₂ phase. The XRD pattern of films deposited from precursor **2** at temperatures between 400 °C and 530 °C is shown in Figure 5.

The highest intensity diffraction peak could be indexed as the (111) plane of SnS. Similarly, the XRD pattern of films deposited using precursors **3** and **4** could also be confirmed as being orthorhombic SnS, with the highest intensity reflection being from the (111) plane. The intensity of peak at 2θ = 33.50° is 40% (400 °C), 8.1% (450 °C), and 1.3% (500 and 530 °C) from films deposited using precursor **3**, and 12.9% (400 °C), 6.6% (450 °C), and 3.8% (500 °C) from films deposited using precursor **4**, relative to the (111) plane of the SnS phase.



Figure 5. XRD pattern of SnS films deposited from [Sn- $(C_4H_9)_2(S_2CN(CH_3)(C_4H_9))_2$] (2) on a glass substrate: (a) 400 °C, (b) 450 °C, (c) 500 °C, and (d) 530 °C. The asterisk symbol (*) denotes the SnO₂ phase.

Rietveld refinements of powder XRD patterns confirm the presence of orthorhombic SnS as a main phase for films deposited from precursors 1-4 with a small amount of SnO₂ phase. Figure 6 displays a representative refinement for the film deposited at 530 °C from precursor **2**. The calculated composition for this film is 89.6 wt % orthorhombic SnS and 10.4 wt % SnO₂ phases, with lattice parameter values of a = 11.197(5) Å, b = 3.997(2) Å, and c = 4.283(1) Å for orthorhombic SnS. The refinement data for films deposited





from precursor 1 at 400 °C exhibit a phase composition of 75.9 wt % SnS and 25.0 wt % SnO₂, with lattice parameters of a = 11.198(4) Å, b = 4.000(4) Å, and c = 4.285(2) Å. The presence of SnO₂ could be due to the aerial oxidation of tin precursors, since samples were handled in open air.

The formation of SnS films in our AACVD experiment indicate the facile reduction of metal center Sn(IV) to Sn(II) in an argon atmosphere.^{13,31} Similar observations have also been reported by Barone et al. during the APCVD experiment using Sn(IV) thiolates as precursors in the presence of H₂S. The authors reported that the stream of H₂S facilitates the reduction of Sn(IV) to Sn(II).³¹

The crystal structure of orthorhombic SnS, SnS₂, and Sn₂S₃ in Figure 7 gives a clear picture about the bonding around



Figure 7. Local Sn environments in (a) SnS, (b) $SnS_{2^{\prime}}$ and (c) Sn_2S_3 ; Sn...S connectivity in (d) SnS, (e) $SnS_{2^{\prime}}$ and (f) Sn_2S_3 . [Color legend: gray, Sn(II); violet, Sn(IV); and yellow, S.] Crystal structure data were obtained from the Inorganic Crystal Structure Database (ICSD) database.

Sn(II) and Sn(IV) ions in different stoichiometries of tin sulfide. The single-crystal X-ray structure of orthorhombic SnS

has been adopted from ref 45. SnS forms a double-layered structure at room temperature. Each Sn(II) ion is bonded to six S atoms in a distorted octahedral geometry. Tin is separated with sulfur through three shorter (ca. 2.7 Å) and three longer (ca. 3.4 Å) distances in an octahedron coordination. In the double-layer structure of SnS, each layer connected with longer Sn-S bonds. It undergoes a transformation from a GeS-type structure to a TlI-type structure above 605 °C with continuous movement of Sn and S along the [100] direction.⁴⁶ Tin disulfide forms the PbI_2 layered structure in which Sn(IV) is in the middle of a perfect octahedron. Each Sn(IV) ion bonded with six S atoms by ca 2.6 Å. In SnS₂ layers, SnS₆ building unit stacked on top of one other along the crystallographic c-axis by weak van der Waals forces. There have been more than 70 polytypes of SnS₂ reported. Sn₂S₃ is a mixed-valence compound with ribbon structure. The Sn(II) ion coordinated with sulfur in a trigonal bipyramidal geometry through Sn-S distances of ca. 2.6 and 2.7 Å. Sn(IV) sites in the ribbon are octahedrally coordinated with Sn-S distances of ca. 2.45-2.60 Å.

The morphology of films deposited using a toluene solution of precursors 1-4 was characterized by scanning electron microscopy (SEM). The SEM images in Figures 8 and 9 show the morphology of films deposited at 400 °C as consisting of a bundle of sheets, consisting of small spherical crystallites with sheets \sim 25–30 μ m in size and sheets 25–30 and 10–15 μ m in size at temperatures of 450 and 500 °C from precursor 1. Similarly, the sheetlike crystallites were deposited from precursors 2, 3, and 4 with considerable variation in size. This gives an idea that variation in the alkyl group on the external coordination zone does not have a profound effect on the decomposition. The morphology of crystallites is different from the films deposited using dithiol, dithiolates, and thiosemicarbazone complexes of Sn(IV) by AACVD.^{13,16} However, spherical crystallites with a sheetlike morphology have been observed in the low-pressure chemical vapor deposition (LPCVD) growth of SnS films.⁴⁷ This indicates that the aerosols of precursor solution does not play a major role in the morphology of SnS films.

The composition of tin and sulfides was analyzed by quantitative energy-dispersive X-ray (EDX) analysis. The



Figure 8. SEM images of SnS films deposited on glass substrates from $[Sn(C_4H_9)_2(S_2CN(C_2H_5)_2)_2]$ (1) at (a) 450 °C and (b) 500 °C; SEM images of SnS films deposited on glass substrates from $[Sn(C_4H_9)_2(S_2CN(CH_3)(C_4H_9))_2]$ (2) at (c) 450 °C and (d) 500 °C.



Figure 9. SEM images of SnS films deposited on glass substrates from $[Sn(C_4H_9)_2(S_2CN(C_4H_9)_2)_2]$ (3) at (a) 450 °C and (b) 500 °C; SEM images of SnS films deposited on glass substrates from $[Sn(C_4H_9)_2(S_2CN(CH_3)(C_6H_{13}))_2]$ (4) at (c) 450 °C and (d) 500 °C.

EDX analysis confirmed the tin:sulfur stoichiometry of films (percentage basis) as 53:47 (400 °C), 56:44 (450 °C), and 58:43 (500 °C) from tin sulfide films deposited using precursor 1; 51:49 (400 °C), 53:47 (450 °C), 56:44 (500 °C), and 59:41 (530 °C) from films deposited using precursor 2; 51:49 (400 °C), 55:45 (450 and 500 °C), and 56:44 (530 °C) from precursor 3; and 55:45 (400 and 450 °C) and 59:41 (530 °C) from precursor 4. The variation in atomic percentage of tin and sulfur in tin sulfide films grown on a glass substrate at different temperatures from a toluene solution of precursors clearly indicates sulfur-deficient films from all precursors. Furthermore, it showed the presence of a small amount of carbon contamination on the films.

The optical band gap of the deposited tin sulfide films can be estimated from the vis-IR spectra. The recorded spectra closely resembled those reported in the literature for SnS.⁷ The optical bandgap of the deposited films is influenced by two factors: the inherent band gap of the material and a tail due to disorder. Bulk SnS has both direct (1.3 eV) and indirect (1.1 eV) band gaps. The band gap of the films was measured from the dependence of absorption coefficient (α) on the photon energy (*hv*). In the present case, a plot of $(\alpha hv)^2$ versus hv is linear, indicating the direct band nature of the films. Extrapolating the linear portion of the curve onto the *x*-axis gives the bandgap for the film (see Figure 10). The evaluated band-gap values are as follows: 1.31 eV (400 °C), 1.36 eV (450 °C), and 1.33 eV (500 °C) for $[Sn(C_4H_9)_2(S_2CN(C_2H_5)_2)_2]$ (1); 1.39 eV (400 °C), 1.21 eV (450 $^\circ C),$ and 1.35 eV (500 and 530 $^\circ C)$ for $[Sn(C_4H_9)_2(S_2CN(CH_3)(C_4H_9))_2]$ (2); 1.21 eV (400 °C), 1.22 eV (450 °C), 1.58 eV (500 °C), and 1.71 eV (530 °C) for $[Sn(C_4H_9)_2(S_2CN(C_4H_9)_2)_2]$ (3); and 1.3 eV (400 °C), 1.38 eV (450 °C), and 1.47 eV (500 °C) for $[Sn(C_4H_9)_2(S_2CN (C_4H_9)_2$ (4). The band gap was found to increase as the deposition temperature increased. It is well-known that the energy band gap of a semiconductor is affected by the residual strain, defects, charged impurities, disorder at the grain boundaries, and also particle size confinement. In addition, the tensile strain will result in a decrease of band gap due to the elongated lattice whereas a compressional strain increases the band gap due to the compressed lattice of the film.⁴⁸ However,



Figure 10. Square of the absorption coefficient $(\alpha h\nu)^2$, as a function of photon energy $(h\nu)$, for SnS film deposited from $[Sn(C_4H_9)_2(S_2CN-(CH_3)(C_4H_9))_2]$ (2) at 400 °C on a glass substrate.

contribution from SnO_2 and carbon impurities to the higherband-gap value of SnS films, in some cases, is not ruled out.

Raman Measurements. Raman spectral studies on selected films deposited using precursors 1-3 at 450 and 530 °C confirms the presence of SnS (see Figure 11). The characteristic Raman bands are seen at the wavenumbers of 95, 161, 190, and 218 cm⁻¹, which agree well with previous observations at 95, 160, 189, and 219 cm⁻¹ for single-crystal SnS.^{49,50} The smaller shift in the observed band position in the present case may be caused by a strain between SnS films and glass substrates. These lines could be assigned to the longitudinal and transverse optic modes of SnS. It is well-known that the Raman lines at 95, 190, and 218 cm⁻¹ correspond to the A_g phonon mode of SnS.

Electrical Measurements. Figure 12 displays the temperature variations of electrical resistivity of films deposited on glass substrates from $[Sn(C_4H_9)_2(S_2CN(C_2H_5)_2)_2]$ (1) at 500 °C and from $[Sn(C_4H_9)_2(S_2CN(CH_3)(C_4H_9))_2]$ (2) at 530 °C and 450 °C. The electrical resistivity of all films exhibits semiconducting behavior with an activation energy at roomtemperature region varying from 0.233 eV for the film



Figure 11. Raman spectra of SnS films deposited from [Sn- $(C_4H_9)_2(S_2CN(C_4H_9)_2)_2$] (1) at 530 °C (red triangles, \triangle) and [Sn($C_4H_9)_2(S_2CN(CH_3)(C_4H_9))_2$] (2) at 450 °C (black squares, \Box), both on glass substrates.



Figure 12. Temperature variation of electrical resistivity of films deposited on glass substrates from $[Sn(C_4H_9)_2(S_2CN(C_2H_5)_2)_2]$ (1) at 500 °C (blue circles, ●), from $[Sn(C_4H_9)_2(S_2CN(CH_3)(C_4H_9))_2]$ (2) at 530 °C (red triangles, ▲), and from $[Sn(C_4H_9)_2(S_2CN(CH_3)-(C_4H_9))_2]$ (2) at 450 °C (green squares, ■).

deposited from precursor **1** to 0.109 and 0.064 eV for films deposited from precursor **2** at 530 and 450 °C, respectively, as shown in the inset in Figure 12. These activation energies correspond well with previously reported values for SnS films^{51,52} and indicate that all three films are extrinsic semiconductors. The room-temperature carrier concentration, mobility, and electrical resistivity values of films are summarized in Table 2. Hall effect measurements confirmed that all films are *p*-type semiconductors with hole concentration in the range of $(0.4-8.6) \times 10^{18}$ cm⁻³ and hole mobility of 0.9–1.4 cm² V⁻¹ s⁻¹. *P*-type conduction in SnS is believed to originate from high concentration of Sn vacancy sites.

The photoconductive response of semiconductor materials is a prerequisite for a material to be considered for solar cell

Table 2. Electrical Properties of Tin Sulfide Films Deposited from Precursor 1 at 500 $^\circ$ C and Precursor 2 at 530 and 450 $^\circ$ C

precursor	deposition temp (°C)	carrier conc, p (× 10 ¹⁸ cm ⁻³)	resistivity, ρ (Ω cm)	mobility, μ (cm ² V ⁻¹ s ⁻¹)
1	500	4.13×10^{17}	10.8	1.4
2	530	3.60×10^{18}	1.58	1.1
2	450	8.64×10^{18}	0.83	0.87

applications. We have investigated the photoconductive response of tin sulfide films deposited from precursors 1-4 at 500 °C by measuring I-V curves using a 633-nm laser lamp. I-V curves of the difference between resistivity values recorded under illumination shown in Figure 13. It is seen that the



Figure 13. Current–voltage characteristics of SnS films under dark conditions (black solid squares, \blacksquare) and illuminated conditions (red solid circles, \bullet) (4.6 mW; 633-nm laser lamp) for films deposited at 500 °C from $[Sn(C_4H_9)_2(S_2CN(C_2H_5)_2)_2]$ (1). Inset show photogenerated current for SnS films deposited from $[Sn(C_4H_9)_2(S_2CN-(C_2H_5)_2)_2]$ (1) (black open squares, \Box) and $[Sn(C_4H_9)_2(S_2CN-(CH_3)(C_4H_9)_2)]$ (2) (red open triangles, \triangle).

gradient of the illuminated I-V curves higher than that of the I-V curve under dark condition. This suggests that the conductivity of the tin sulfide films become high under illumination that is due to photoinduced carriers. I-V measurement also showed linear data without any rectification behavior, which indicates the absence of a Schottky barrier at Ag/SnS contacts. The observed photosensitivities of tin sulfide films deposited at 500 °C from the dibutyl derivative of tin precursors are 0.4% for 1, 2.1% for 2, 1.2% for 3, and 1.0% for 4.

CONCLUSIONS

A series of diorganotin complexes of dithiocarbamates, including $[Sn(C_4H_9)_2(S_2CN(RR')_2)_2]$ (R, R' = ethyl (1); R = methyl, R' = butyl (2); R, R' = butyl (3); R = methyl, R' = hexyl (4); and $[Sn(C_6H_5)_2(S_2CN(RR')_2)_2]$ (R, R' = ethyl (5); R = methyl, R' = butyl (6); R, R' = butyl (7); R = methyl, R' =hexyl (8) have been synthesized. The structures of 2, 3, and 8 were determined by single-crystal X-ray crystallography. Thermogravimetric analysis (TGA) showed single-step decomposition of complexes 1, 3, and 5-8 and double-step decomposition of complexes 2 and 4 at temperatures between 195 °C and 325 °C. Complexes 1-4 were used as single-source precursors for the deposition of tin sulfide thin films by aerosolassisted chemical vapor deposition (AACVD) at temperatures of 400-530 °C. Complexes 1-4 primarily deposited the orthorhombic SnS phase. Rietveld analysis on the powder diffraction patterns appears to indicate the presence of some SnO₂. The films consist of sheetlike crystallites. The measured bandgap of the films varied between 1.2 eV and 1.7 eV. Distinct Raman bands at 95, 161, 190, and 218 cm⁻¹ confirmed the presence of the orthorhombic SnS phase. The results of SnS films deposited from precursors 1-4 are given in Table 3. The highest photosensitivity (2.1%) was observed from films deposited using precursor 2 at 500 °C.

Table 3. Summary of Band Gap, Relative Intensity of SnO₂ XRD peak at 33.5°, EDX Data, and Morphology of Films Obtained from Precursors 1–4 at Different Temperatures

			EDX (%)				
$\underset{(^{\circ}C)}{temp, } T$	band gap (eV)	XRD peak at $(2\theta) = 33.5^{\circ}$ (%)	Sn	S	morphology		
$[Sn(C_4H_9)_2(S_2CN(C_2H_5)_2)_2] (1)$							
400	1.31	16.4	53	47	bundle of sheets		
450	1.36	16.3	56	44	sheets		
500	1.33	1.1	58	43	bundle of sheets		
$[Sn(C_4H_9)_2(S_2CN(CH_3)(C_4H_9))_2] (2)$							
400	1.39	7.3	51	49	sheets		
450	1.21	3.4	53	47	bundle of sheets		
500	1.35	5.3	56	44	bundle of sheets		
530	1.35	2.9	59	41	bundle of sheets		
	[Sn	$(C_4H_9)_2(S_2CN(C_4H_9)_2)$)2] (3)				
400	1.21	40	51	49	sheets		
450	1.22	8.1	55	45	sheets		
500	1.58	1.3	55	45	sheets		
530	1.71	1.3	56	44	sheets		
$[Sn(C_4H_9)_2(S_2CN(CH_3)(C_6H_{13}))_2] (4)$							
400	1.3	12.9	55	45	bundle of sheets		
450	1.38	6.6	55	45	bundle of sheets		
500	1.47	3.8	59	41	bundle of sheets		

ASSOCIATED CONTENT

S Supporting Information

Crystallographic information files (CIF) for complexes 2, 3, and 8 as electronic copies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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