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Atmospheric pressure chemical vapour deposition of tin(II) sulfide films on glass substrates from $Bu^n{}_3SnO_2CCF_3$ with hydrogen sulfide

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In a search for a mild, rapid, moderately low temperature route to the deposition of thin films of tin(II) sulfide (SnS) on glass, we have investigated the APCVD reaction of tri-*n*-butyltin trifluoroacetate with hydrogen sulfide at 350–600 °C under nitrogen. The films deposited over a 15 min period were shown to be SnS by X-ray diffraction, Raman microscopy, EDAX, SEM and XPS. The conditions established are attractive for the large scale, rapid production of tin(II) sulfide films.

Many phases of tin sulfide have been reported, the most common being tin(II) and tin(IV) sulfides;[1] others include Sn_2S_3, Sn_3S_4 and Sn_4S_5.[1] Of these compounds, tin(II) sulfide has attracted the most interest in recent years. Its optical band gap of 1.3 eV is intermediate between those of gallium arsenide and silicon,[2] which gives it potential for use as a holographic recording medium,[3] as part of a solar collector,[2] as a photovoltaic material[4] and as a solar control coating.[5] Tin(II) sulfide, which is grey/black,[6] adopts a distorted sodium chloride structure and is isomorphous with germanium sulfide.[7]

A wide range of preparative routes has been used to form bulk tin(II) sulfide, including pyrolysis of either $(R_3Sn)_2S$ or cyclic $(R_2SnS)_3$ (R = benzyl, phenyl).[8–10] These reactions produce mixtures of SnS and tin metal. Room temperature synthesis from the elemental reaction of tin metal and sulfur in liquid ammonia produce 60% SnS, 35% SnS_2 and 5% unreacted tin.[6] Thin films of SnS have been produced by chemical vapour deposition (CVD) techniques. CVD of $SnCl_4$ with H_2S in a hydrogen plasma[2] produces films of SnS in the temperature range 100–300 °C. At 100 °C there is a large amount of contamination by $SnCl_2$, $SnCl_4$ and sulfur. At 150 °C a small amount of sulfur and $SnCl_2$ is still present, but films deposited at 200 °C and above show little contamination (as assessed by X-ray techniques). The contamination was attributed to the adsorption of radicals produced from H_2S and $SnCl_4$ onto the surface. Higher temperatures facilitated desorption of these contaminants and so minimised chlorine incorporation into the film. At 250 °C there was a preferential growth in the diffraction peaks of the [111] planes. The optimum conditions produced films with a tin to sulfur ratio of $SnS_{0.75}$ determined by EDAX. The atmospheric pressure CVD (APCVD) reaction of $SnCl_4$ with H_2S[11] produces SnS_2 at temperatures between 300 and 450 °C. At temperatures in excess of 550 °C films of SnS are deposited and at intermediate temperatures Sn_2S_3 is formed. No other phases were observed by X-ray diffraction or Raman microscopy. The CVD reaction of tetraethyltin with hydrogen sulfide produces films which are yellow-orange when thin, but grey when thicker (*ca.* 3 µm).[12] It was reported that the coating was most likely to be SnS owing to the reducing atmosphere of hydrogen used in the synthesis. However, it has been shown that thin (<0.5 µm) films of SnS_2 are yellow, while >2 µm films of SnS_2 are black.[11] Films of tin sulfide have also been produced by deposition reactions including the electroless deposition from a mixture of $SnCl_2 \cdot 2H_2O$ in acetone, thioacetamide in distilled water, aqueous ammonia and triethanolamine[13] and deposition from the dipping of glass slides alternately into cold Na_2S and hot $SnCl_2$.[14] Passing hydrogen sulfide through tin(II) chloride in hydrochloric acid produces a yellow precipitate, which may then be evaporated onto glass slides and annealed in vacuum to produce tin(II) sulfide.[15]

Chemical vapour deposition is a versatile technique for the deposition of thin films and is widely used in the semiconductor industry. APCVD is used in commercial glass production, since appropriate heads may be attached directly to float glass lines. The advantage of APCVD is that films may be deposited in relatively short times (seconds/minutes for APCVD compared with hours for LPCVD). Tri-*n*-butyltin trifluoroacetate ($Bu^n{}_3SnO_2CCF_3$) has previously been used as an APCVD precursor for producing fluorine-doped tin oxide films.[16] The fluorine doping (*ca.* 0.5% or less) improves the solar-control properties of tin oxide films. At the outset of this study it was thought that this precursor, when used with hydrogen sulfide gas, would produce tin sulfide films, which may incorporate fluorine.

Here, we report the APCVD reaction of tri-*n*-butyltin trifluoroacetate with hydrogen sulfide. The films were analysed by XRD, Raman, Scotch-tape tests, EDAX, SEM and XPS. We are interested in tin(II) sulfide because of its importance as a semiconducting material, and in developing low temperature routes to its deposition onto glass substrates. Previous APCVD work[11] has led to the formation of tin(II) sulfide from $SnCl_4$ and H_2S only at temperatures in excess of 550 °C.

Experimental

General

Starting materials and solvents were obtained from Aldrich and used as supplied without further purification. Hydrogen sulfide and nitrogen gases were purchased from BOC and used as supplied. Tri-*n*-butyltin trifluoroacetate was synthesised as outlined below. SiCO-coated glass supplied by Pilkington Glass plc. was used as the substrate. X-ray diffraction measurements were carried out on a Philips XPert θ–2θ diffractometer. Cu-Kα radiation was used in the reflection mode with PC-APD version 4.0b software. Both the Cu-Kα_1 and Cu-Kα_2 lines were present. Patterns were indexed using UnitCell.[17] SEM and EDAX were obtained using a Hitachi

S570 Filament scanning electron microscope, with a beryllium window. EDAX analyses were standardised relative to cobalt metal. EDAX data were quantified using the Oxford Instruments AM10,000 software package. Raman spectroscopy was carried out using a Dilor Infinity Raman spectrometer with a notch filter and a CCD detector coupled to an Olympus microscope. An excitation line wavelength of 632.8 nm from a HeNe laser was used and spectra were calibrated against neon emission lines. X-Ray photoelectron spectra were recorded with a VG ESCALAB 220I XL instrument using monochromatic Al-Kα radiation at a pass energy of 20 eV and a spot size of 300 µm. Depth profiling was carried out using an Ar^+ ion gun for two 6 min etches. DSC measurements on tri-*n*-butyltin trifluoroacetate were measured on a Shimadzu DSC-50 apparatus from 25 to 700 °C with a 10 °C min^{-1} ramp rate.

Synthesis of tri-*n*-butyltin trifluoroacetate

Tri-*n*-butyltin trifluoroacetate[18] was prepared by refluxing 3.83 g (28 mmol) sodium trifluoroacetate with 9.14 g (28 mmol) tri-*n*-butyltin chloride in 0.12 dm^3 ethanol for 2 h. The ethanol was removed *in vacuo* and the resultant white solid recrystallised from diethyl ether. This yielded colourless crystals in 68% yield with melting point of 49–50 °C.

Chemical vapour deposition reactions

APCVD reactions were carried out on a horizontal-bed cold-walled reactor. Four independent gas lines were used. Valves containing VESPEL inserts were used to direct gas flows to and away from the reactor. The full details of the reactor have previously been reported.[5,11] SiCO-coated glass was cleaned by being wiped with light petroleum (bp 40–60 °C), washed with propan-2-ol and dried in air. 99.7% Hydrogen sulfide gas was used as supplied by BOC. Nitrogen (99.99%) was the diluent gas in the system and used as supplied by BOC. The stainless steel gas lines and glass in the reactor were heated under a constant flow of nitrogen (1 dm^3 min^{-1} through each line).

The temperature of the glass substrate was varied between 300 and 600 °C. The gas lines were heated to 150 °C. When the required temperatures were attained, the system was left for a few minutes to reach thermal equilibrium. The $Bu^n{}_3SnO_2CCF_3$ in the bubbler was heated to *ca.* 130 °C. Nitrogen flows in all lines were increased and hydrogen sulfide (0.6 dm^3 min^{-1}) admitted to the system. Nitrogen (0.4 dm^3 min^{-1}) was then passed through the bubbler and $Bu^n{}_3SnO_2CCF_3$ vapour incorporated into the gas stream. The total gas flow through the reactor was 12.2 dm^3 min^{-1}. The four-way valve was turned and the gas streams were allowed to mix *ca.* 4 cm before reaching the reactor chamber. Run times of 15 min were marked by the turning of the four-way valve at the start and end. After the reaction, the bubbler was closed and the hydrogen sulfide flow stopped. The heaters were turned off and the lines, glass and reactor allowed to cool to room temperature under a 1 dm^3 min^{-1} flow of nitrogen.

Results and discussion

The conditions for all the APCVD reactions of tri-*n*-butyltin trifluoroacetate with hydrogen sulfide were identical with the exception of the substrate temperature. The run conditions are summarised in Table 1. The coater temperature was varied from 300 to 600 °C in increments of 50 °C. No coating was formed with a substrate temperature of 300 °C, and the film deposited at 350 °C for 15 min was very thin. All films were grey. Films passed the Scotch tape test, but could be removed by scraping with a scalpel. The band gap of the film deposited at 450 °C was measured and found to be 1.5 eV (lit.[2,19] 1.08–1.3 eV).

Table 1 Reaction conditions for all runs

Run time	15 min
Growth rate	50 nm min^{-1}
Nitrogen flow through bubbler	0.4 dm^3 min^{-1}
Bubbler temperature	130 °C
Total nitrogen flow through reactor	11.6 dm^3 min^{-1}
Hydrogen sulfide flow through reactor	0.6 dm^3 min^{-1}

The X-ray diffraction pattern of the film deposited at 450 °C is shown in Fig. 1. This corresponds closely to the diffraction pattern of tin monosulfide as reported by Boudjouk *et al.*[8–10] The unit cell parameters were found to be $a = 11.27(4)$, $b = 3.972(6)$, $c = 4.24(1)$ Å (*cf.* $a = 11.18–11.21$, $b = 3.98–4.02$, $c = 4.30–4.33$ Å determined by Boudjouk *et al.*[8–10]). This reflects a slight decrease in the unit cell volume of 2%. XRD did not show contamination by any other phase such as tin disulfide, tin or sulfur.

The Raman spectra for all films were recorded using 632.8 nm excitation, the spectrum recorded from the film deposited at 450 °C being shown in Fig. 2. A previous report[20] on tin(II) sulfide indicates that the A_g modes give rise to bands at 95 and 192 cm^{-1} together with a very weak band at 218 cm^{-1}; other bands occur at 164 cm^{-1} (B_{3g}), 208 cm^{-1} (weak, B_{1g}) and 290 cm^{-1} (B_{2g}). The pattern recorded from the film deposited at 450 °C (Fig. 2) corresponds exactly to tin(II) sulfide crystallites with random orientation.[20] No evidence of contamination by tin, sulfur or other phases of tin sulfide was found by Raman analysis, this technique being particularly sensitive to free sulfur.

EDAX showed that the Sn:S ratio in the film deposited at all temperatures was approximately 1 : 1 within the error limits of the apparatus. Some breakthrough of the excitation volume to the underlying glass was observed (*ca.* 2 µm depth). This, together with the SEM work, indicated that the films were of the order of 200–500 nm thick. The SEM image of the film deposited at 450 °C is shown in Fig. 3 in which it is evident that the film is made up of cuboids approximately 0.5–1 µm across. This morphology is observed in all films produced in this study. It is, however, dissimilar to films deposited from tin tetrachloride with hydrogen sulfide *via* APCVD.[11] The particle size is the same, but the films deposited from $Bu^n{}_3SnO_2CCF_3$ with H_2S are composed of angular crystallites rather than wavy agglomerates as was observed in the deposition from $SnCl_4$ with H_2S.

The film deposited at 450 °C from the reaction of $Bu^n{}_3SnO_2CCF_3$ with H_2S was analysed by XPS. Although the surface was heavily contaminated with carbon and oxygen, the bulk composition showed less oxygen and almost no carbon. Fluorine was not observed in the film. Two tin environments were observed with binding energies of 485.9 and 484.8 eV, the former giving rise to a significantly more pronounced peak than the latter. The binding energy of tin

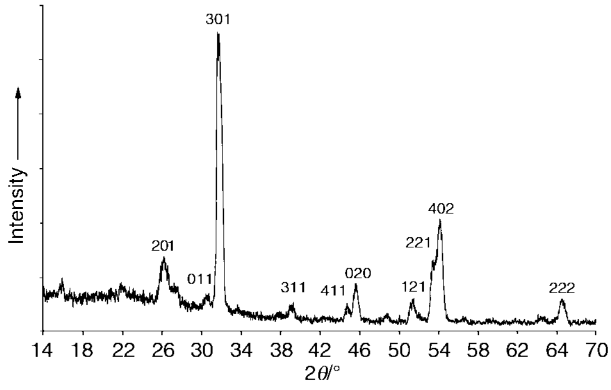

Fig. 1 Glancing angle X-ray diffraction pattern for the film obtained from the reaction of $Bu^n{}_3SnO_2CCF_3$ with H_2S at 450 °C (10 most intense peaks indexed).

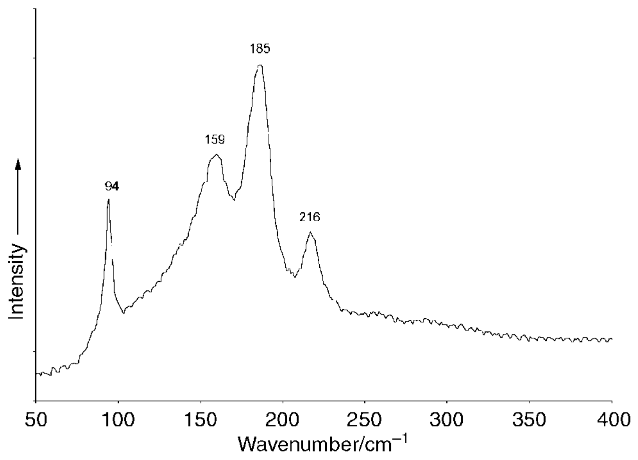

Fig. 2 Raman spectrum of the film deposited at 450 °C from the reaction of $Bu^{n}{}_{3}SnO_{2}CCF_{3}$ with $H_{2}S$.

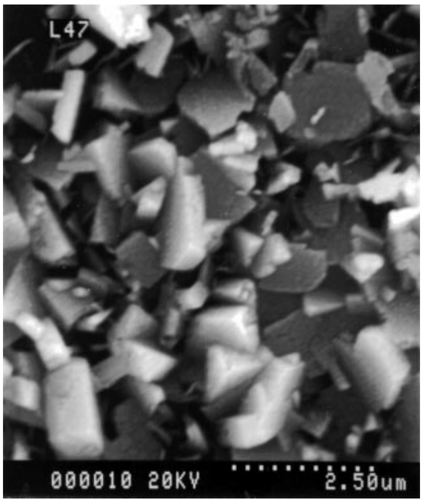

Fig. 3 Scanning electron micrograph of the film obtained from the reaction of $Bu^{n}{}_{3}SnO_{2}CCF_{3}$ with $H_{2}S$ at 450 °C.

in SnS is 485.6 eV,[21] so the first of these peaks is most likely due to tin(ii) sulfide. The Sn $3d_{5/2}$ binding energy in tin(ii) oxide is 486.9 eV[22] and in tin(iv) oxide is 486.6 eV.[23] The second environment observed for tin is likely to be tin metal, which has a binding energy of 484.9 eV.[24] This peak could be a result of preferential sputtering of sulfur during etching leaving some exposed tin metal. This effect has been observed in an XPS study of tin nitride films where preferential sputtering caused all the nitrogen to be removed, leaving tin metal.[25] The binding energy observed for sulfur occurred at 161.1 eV characteristic of sulfur in a metal sulfide (*cf.* a similar binding energy for sulfur of 161.7 eV[26] in ZnS). The oxygen observed in the bulk of the material had a binding energy of 533.4 eV which is not due to a metal oxide for which the characteristic binding energies are in the region 529–532 eV [that for tin(iv) oxide is 530.6 eV[27] and for water is 533.1 eV[28]]. Other molecular oxygen species also have binding energies in this vicinity. In a previous study of tin sulfides deposited by APCVD from tin tetrachloride and hydrogen sulfide[11] or tin tetrabromide and hydrogen sulfide[29] very little oxygen was observed in the bulk of the film by XPS. Although the oxygen may arise from handling and storing the samples in air—the films are porous and may absorb water from the air—comparison with previous work where films were also handled in air suggests that the oxygen arises during the reaction, possibly from the starting material.

The XRD, Raman, EDAX and XPS measurements all indicate that the predominant phase formed by the reaction of $Bu^{n}{}_{3}SnO_{2}CCF_{3}$ with $H_{2}S$ is tin(ii) sulfide. This is interesting, since the starting material was a tin(iv) compound. A number of examples of tin(iv) precursors forming tin(ii) sulfide have been reported. The majority of these involved forming bulk materials, although some thin films of SnS were deposited. Among these is the work of Ortiz *et al.*[2] whose plasma-enhanced CVD reactions of tin tetrachloride and hydrogen sulfide resulted in tin monosulfide being formed. This was attributed to the reducing atmosphere provided by the hydrogen carrier gas. Mansevit and Simpson[12] also formed tin(ii) sulfide by CVD, this time using tetraethyltin with hydrogen sulfide. The diluent gas in this experiment was hydrogen and this was, again, thought to be the cause of the reduction in oxidation state. Parkin and coworkers[11] deposited tin(ii) sulfide from tin(iv) chloride and hydrogen sulfide by APCVD, but this phase was only formed at temperatures in excess of 550 °C. This is due to the fact that the Gibbs free energy of formation of tin(ii) sulfide is lower than that of tin(iv) sulfide at higher temperatures, tin(iv) sulfide being favoured at lower temperatures. The same group also studied the reaction of tin tetrabromide with hydrogen sulfide.[29] Again, tin(ii) sulfide was only formed at temperatures in excess of 500 °C, the actual temperature being dependent on the hydrogen sulfide flow through the system. It was found that higher $H_{2}S$ flows led to tin(ii) sulfide deposition at lower temperatures, but flows up to 1.2 $dm^{3}\,min^{-1}$ could only deposit SnS above 500 °C. Boudjouk *et al.*[8–10] formed tin(ii) sulfide by the bulk decomposition reaction of $(R_{3}Sn)_{2}S$ and cyclic $(R_{2}SnS)_{3}$ (R = Bn, Ph). In this case, reduction of the metal occurs because the phenyl or benzyl groups are good leaving groups. The decomposition mechanism is thought to start with an aryl group migrating to a chalcogenide atom thus leaving the tin in the +2 oxidation state. Tin(ii) and tin(iv) sulfides produced by room temperature synthesis in liquid ammonia[6] were heated to 300–350 °C, leading to the formation of tin(ii) sulfide only. In the case of tri-*n*-butyltin trifluoroacetate, the formation of tin(ii) compounds is not unexpected. They may have formed as a consequence of decomposition of the starting material to a tin(ii) species in the gas phase before adsorption onto the glass. This would be in accordance with the result produced by Boudjouk *et al.*[8–10] The fact that no fluorine is observed in the XPS measurements indicates that the ligand is completely lost during the decomposition. There is a possibility that the starting material reacts with the $H_{2}S$ to form $(Bu^{n}{}_{3}Sn)_{2}S$ which may then undergo the same reaction as observed by Boudjouk *et al.*[8–10] This group only observed decomposition at temperatures above 300 °C, which would be consistent with our results where films could not be deposited below 350 °C. The by-product, in this case, would be $CF_{3}CO_{2}H$, which can be used to dope fluorine into films. It may be that the reaction time of 15 min is sufficiently long that any tin(iv) sulfide produced would be reduced to tin(ii) sulfide accompanied by the evolution of sulfur, as found by Shaw and Parkin.[6] This mechanism is unlikely, however, as heating previously deposited films of SnS_{2} under N_{2} or $H_{2}S$ for 15 min periods does not result in reduction until a temperature of 450 °C is reached.[30] A further possibility is that tri-*n*-butyltin trifluoroacetate decomposes on contact with the glass to give tin oxide, this being subsequently converted to the sulfide by the large excess of hydrogen sulfide in the system. We have shown that heating thin films of tin oxide in the presence of $H_{2}S$ leads to the corresponding sulfide being produced.[30] This would mean that if the precursor were to decompose to tin(iv) oxide, $H_{2}S$ would react with this to give tin(iv) sulfide. Consequently, it is believed that the precursor is reduced to tin(ii) before the film is deposited. Very little oxygen was found in the tin sulfide films produced by APCVD from tin tetrachloride with hydrogen sulfide.[11] As the nature of by-products has not been studied, it is currently impossible to determine whether these or other mechanisms are occurring.

A significant result was the absence of fluorine observed in the XPS (*ca.* 0.5% detection limit). Other techniques would have to be employed to detect any fluorine present. The presence of oxygen in the films may account for the minor alteration in unit cell volume as observed by X-ray diffraction.

In summary, we have shown that it is possible to form tin(II) sulfide from tri-*n*-butyltin trifluoroacetate with hydrogen sulfide using significantly lower temperatures than required by APCVD techniques previously used. Other groups working on forming tin(II) sulfide *via* LPCVD have succeeded at these lower temperatures, but only with a reducing hydrogen atmosphere or by employing plasma enhanced CVD. The films produced here have been characterised by Raman, X-ray diffraction, EDAX, XPS and band gap measurements. All analytical techniques indicate that SnS is the only phase observed, except for XPS which indicates that a small amount of water may be present in the films. This is probably due to the porosity of the films as can be seen from the SEM image in conjunction with their being handled in air.

Conclusions

Thin films may be deposited from the chemical vapour deposition reaction of $Bu^n{}_3SnO_2CCF_3$ with hydrogen sulfide. X-Ray diffraction, Raman microscopy and X-ray photoelectron spectroscopy all concur that the predominant phase formed is tin(II) sulfide. The conditions employed in this study are milder and use lower temperatures than conditions used to form tin(II) sulfide in previous work.

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