Atmospheric Pressure Chemical Vapor Deposition of Tin Sulfides (SnS, Sn_2S_3, and SnS_2) on Glass

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Atmospheric pressure chemical vapor deposition of SnS_2, Sn_2S_3, and SnS has been achieved onto glass substrates from the reaction of $SnCl_4$ with H_2S at 300−545 °C. The films show good uniformity and surface coverage, adherence, and a variety of colors (black, yellow, brown, and gray) dependent on deposition temperature and film thickness. Growth rates were on the order of 1−2 μm min^{-1}. All the films were crystalline. For substrate temperatures of up to 500 °C single phase films with the hexagonal SnS_2 structure (a = 3.65(1) Å, c = 5.88(1) Å) were formed. At 525 °C a film of mixed composition containing predominantly orthorhombic Sn_2S_3 (a = 8.83(1) Å, b = 3.76(1) Å, c = 14.03(1) Å) was formed together with some SnS_2. At 545 °C films with orthorhombic SnS structure (a = 4.30(1) Å, b = 11.20(1) Å, c = 3.99(1) Å) were formed. Scanning electron microscopy (SEM) revealed a variety of different film thicknesses and morphologies, including needles, plates, and ovoids, dependent on the deposition temperature and time. Energy-dispersive X-ray analysis (EDX) and electron probe measurements on the films indicated elemental ratios close to those for tin disulfide ($SnS_{1.98}$), ditin trisulfide ($SnS_{1.60}$), and tin monosulfide ($SnS_{1.10}$) and revealed no incorporation of chlorine. X-ray photoelectron spectroscopy (XPS) gave results in agreement with those from EDX and revealed binding energies of Sn $3d_{5/2}$ = 486.5(1) eV and S 2p = 161.6(2) eV for films grown at less than 500 °C (SnS_2), and Sn $3d_{5/2}$ = 485.7 (1) eV and S $2p_{3/2}$ = 161.0 eV for the film grown at 545 °C (SnS). Raman microscopy showed that the films of SnS_2 had bands at 315 and 215 cm^{-1}, those of Sn_2S_3 had bands at 307, 251, 234, 183, 71, 60, and 52 cm^{-1}, and those of SnS had bands at 288, 220, 189, 163, and 96 cm^{-1}. The band gap of SnS_2 was 2.14 eV. Sheet resistance measurements showed that all of the films were essentially insulating.

Introduction

Tin forms a variety of sulfides, SnS_2, Sn_2S_3, Sn_3S_4, Sn_4S_5, SnS, and numerous polysulfide anions.[1] The two most important tin sulfides are SnS, which has a distorted GeS structure,[2] and SnS_2, which adopts a PbI_2 layer structure;[3] both materials are semiconductors with band gaps of 1.3 and 2.18 eV, respectively.[4,5] Tin monosulfide in particular has attracted some attention because its band gap nestles between those of Si (1.12 eV) and GaAs (1.43 eV). Thin films of tin monosulfide have been investigated for use in holographic recording media,[6] as part of solar collectors,[7] and as photovoltaic materials with high conversion efficiency.[8] They also have potential as heat mirrors in solar control coatings.[9] Tin(II) sulfide has relatively useful thermal and hydrolytic stability, low toxicity, and relatively low cost.[10] Tin(IV) disulfide was first synthesized some 200 years ago[11] and has more than 70 polytype structures.[12] This material has an hexagonal close-packed structure within the SnS_2 layer but different c parameters orthogonal to the layer. The c parameter was found to be a multiple of the interlamellar spacing (5.899 Å).[13]

Bulk tin chalcogenides have been synthesized from the elements by repeated mixing and heating to high temperatures,[14] reactions in liquid ammonia,[15] decom-

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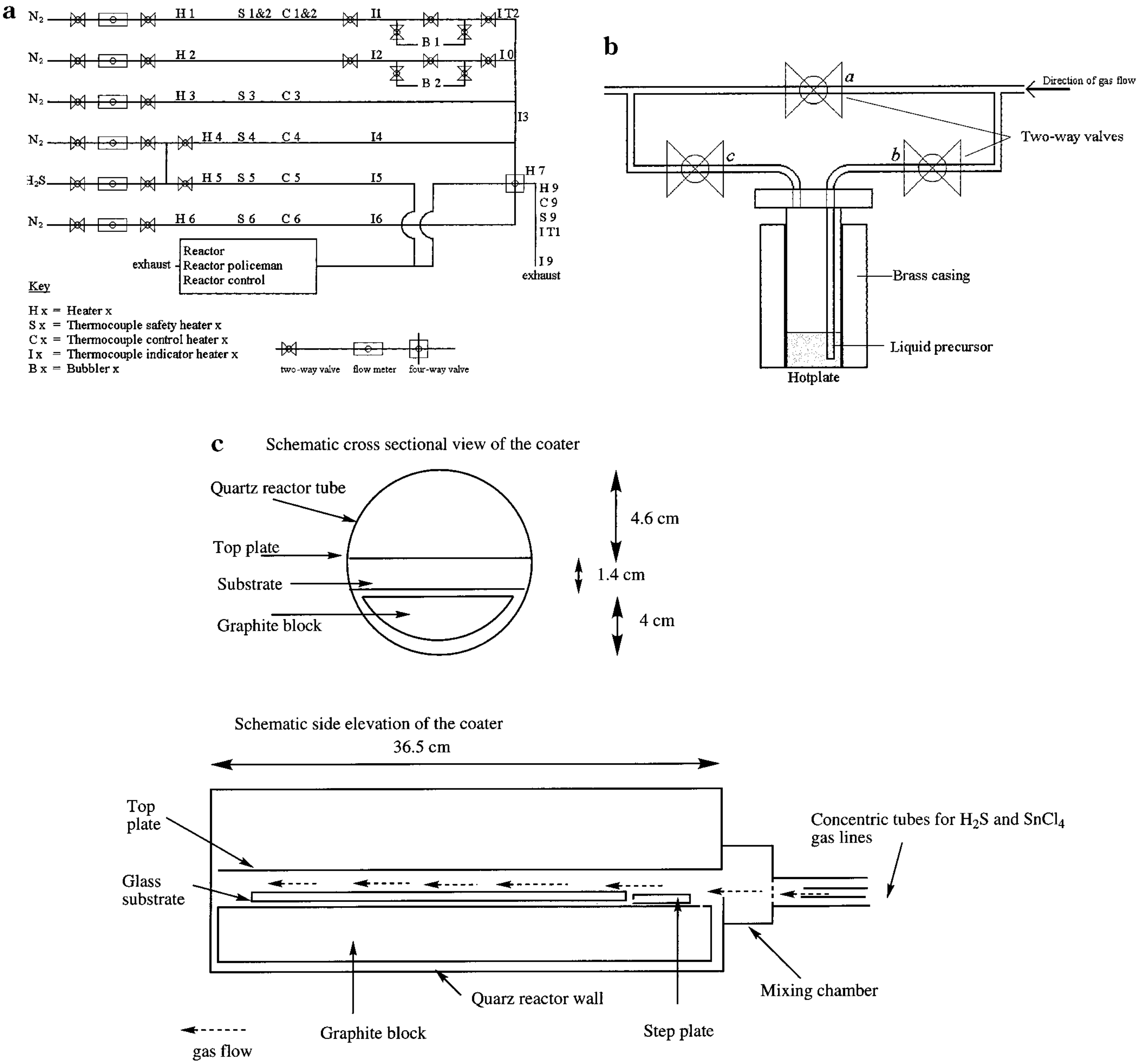

Figure 1. (a) Schematic line diagram of the APCVD rig, (b) schematic representation of the bubbler design, and (c) reactor dimensions.

position of molecular precursors such as $(Ph_2SnS)_3$,[16] solid-state metathesis,[17] organic template mediated reactions,[18] and the reaction of H_2S on the metal oxide.[19] Single crystals of SnS_2 have been obtained by the vapor transport method.[20] Thin films of tin sulfides have been grown by spray pyrolysis,[21] melt growth,[22] chemical baths,[23] and electrodeless deposition.[10] There have been very few reports of growing SnS and SnS_2 films by low-pressure chemical vapor deposition (CVD) either from organometallic precursors[24] or from plasma-enhanced processes.[25] The plasma-enhanced CVD reaction of $SnCl_4$ and H_2S at 100−300 °C and low pressure on small silica substrates (1 cm × 2 cm) produces SnS films that are heavily contaminated with chlorine and sulfur. Under optimum conditions the films had a tin to sulfur ratio of $SnS_{0.8}$ and a band gap of 1.16 eV. Organometallic precursor routes to tin sulfide involve the formation of films on CaF_2 and MgF_2 substrates by reaction of tetramethyl- or tetraethyltin with hydrogen sulfide and

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Table 1. APCVD Reaction Conditions, Color, Morphology, EDX, and XRD Analysis of the SnS_x Films on Glass Prepared by Reaction of H_2S with $SnCl_4$

temp/°C		gas flow/ $dm^3\ min^{-1}$							indexed X-ray data		
coater	bubbler	N_2	H_2S	run time/s	color of film	film morphology (SEM)	elemental composition (EDX)	phase seen by X-ray	*a*/Å	*b*/Å	*c*/Å
300	76	1.2	0.6	180	black	needles	$SnS_{1.96}$[c]	SnS_2	3.67		5.66
300	74	1.5	0.3	30	yellow	needles	$SnS_{1.98}$[c]	SnS_2	3.62		5.73
350	80	1.5	0.3	30	pale yellow	plates	$SnS_{2.20}$				
400	73	1.5	0.3	30	yellow	plates	$SnS_{2.16}$	SnS_2	3.63		5.80
445	67	1.5	0.3	30	yellow	plates	$SnS_{2.04}$				
495	74	1.5	0.3	30	yellow	plates	$SnS_{2.08}$	SnS_2	3.65		5.88
525	81	1.5	0.3	30	gray/yellow	plates[a]	$SnS_{1.60}$	Sn_2S_3	8.83	3.75	14.03
545	75	1.5	0.3	30	gray	agglomerate	$SnS_{1.10}$[b]	SnS	11.20	3.99	4.30

[a] SEM revealed that the SnS_x film looks to be a mixture of plates and agglomerates. [b] Elemental analysis determined by XPS. [c] Elemental ratio determined from electron probe measurements.

hydrogen at 600 °C. No characterization data were reported except for film color (yellow and gray) and thickness. The authors speculated that SnS was formed because of the reducing conditions.[24]

We have an interest in forming films by atmospheric pressure chemical vapor deposition (APCVD) for solar-control and self-cleaning applications.[26] APCVD is a particularly attractive method of coating glass substrates as it has fast growth rates and the appropriate heads can be added directly to commercial float-glass manufacturing lines. The coating is applied to the glass at ca. 500−600 °C as it cools on a bed of molten tin. Here we report a detailed APCVD study of the reaction of $SnCl_4$ and H_2S on glass.

Experimental Section

Nitrogen (99.99%) and H_2S (99.9%) were obtained from BOC and used as supplied. Coatings were obtained on SiCO-coated glass. APCVD experiments were conducted on 225 mm × 89 mm × 4 mm pieces using a horizontal-bed cold-wall APCVD reactor (Figure 1a). The glass was cleaned by being washed with petroleum ether (60−80) and 2-propanol. The glass was heated by four Whatman cartridge heaters that were inserted into a flat-bed graphite block, the temperature of which was monitored by a Pt−Rh thermocouple. Thermocouple measurements indicated that temperature gradients of less than 10 °C at 500 °C occurred across the glass substrates. The rig was designed so that six independent gas lines could be utilized. All gas handling lines, regulators, and flow valves were made of stainless steel and had $^1/_4$ in. internal diameter except for the inlet to the mixing chamber and for the exhaust line from the apparatus which had $^1/_2$ in. i.d. In these experiments four gas lines were used, three for nitrogen and one for nitrogen/hydrogen sulfide. The gases which came directly from a cylinder were preheated by being passed along 2 m lengths of stainless steel tubing wrapped in heating tape and insulation. The temperatures of all the gas inlet lines were monitored by Pt−Rh thermocouples and Eurotherm heat controllers. Tin(IV) chloride (99.9%, Aldrich Chemical Co.) was used as supplied and placed into a stainless steel bubbler (Figure 1b). The bubbler was heated between 60 and 90 °C by a hot plate, and $SnCl_4$ was introduced into the gas streams by passing hot nitrogen gas through the liquid. The nitrogen-diluted $SnCl_4$ stream and H_2S streams were mixed by using concentric pipes of $^1/_4$ in. and $^1/_2$ in. diameter. The inner pipe was 3 cm shorter than the outer pipe, which was attached directly to the mixing chamber of the coater. 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 nitrogen at 150 °C for 3 h before and after each run. Suitable two- and four-way valves (containing VESPEL inserts and rated to 200 °C) allowed the nitrogen lines to be diverted into or away from the bubblers (Figure 1a). Deposition experiments were conducted by heating the horizontal bed reactor and the bubbler to the required temperatures before diverting the nitrogen line through the bubbler and hence to the reactor (Table 1). Deposition experiments were timed by stop watch and were either 30 s or 3 min. At the end of the deposition the bubbler line was closed and only nitrogen gas was 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 XPS, EDX, SEM, electron microprobe and UV studies. Large pieces of glass (ca. 4 cm × 4 cm) were used for sheet resistance, X-ray diffraction, Raman, and Scotch tape tests.

X-ray diffraction patterns were measured on a Philips X-pert diffractometer using unfiltered Cu Kα ($\lambda_1 = 1.5045$ Å, $\lambda_2 = 1.5443$ Å) radiation in the reflection mode using a glancing incident angle. Samples were indexed using Unit Cell[27] and compared to database standards, some preferred orientation being observed for the films. SEM/EDX was obtained on a Hitachi S570 instrument using the KEVEX system. Electron microprobe analysis was obtained on a JEOL EMA and referenced against sulfur and tin standards. X-ray photoelectron spectra were recorded with a VG ESCALAB 220i XL instrument using focused (300 μm spot) monochromatic Al Kα radiation at a pass energy of 20 eV. Scans were acquired with steps of 50 meV. A flood gun was used to control charging, and the binding energies were referenced to an adventitious C 1s peak at 284.8 eV. Depth profile measurements were obtained by using argon beam sputtering. UV−vis spectra were recorded in the range 200−1000 nm using a Shimadzu double beam instrument, and band gaps were calculated by the direct method. Raman spectra were acquired using an Olympus BH-2 microscope coupled to either a Dilor XY triple-grating spectrometer or a Renishaw Raman System 1000. The Dilor system used an excitation line wavelength of 647.1 nm from a Coherent Innova 300 Kr^+ laser. The Renishaw system used a helium−neon laser of wavelength 632.8 nm. Both Raman systems were calibrated against the emission lines of neon.

Caution: Hydrogen sulfide is toxic; the whole APCVD apparatus was contained within a fume cupboard. Large build-ups of particulate matter from prereaction could conceivably block the gas exhaust pipe from the reactor. The exhaust pipe was consequently made of $^1/_2$ in. diameter stainless steel and heated. The glass coater was surrounded by a wire cage.

Results

Reaction of tin(IV) chloride with hydrogen sulfide on substrates heated to 300−545 °C under APCVD condi-

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tions produced tin sulfide films of different colors and compositions (Table 1). No films could be grown from 25 to 200 °C from this system. At temperatures above 200 °C and below 300 °C brown films could be grown, although the growth rates were relatively slow. The majority of reactions studied were standardized for constant flow rates and 30 s duration, these conditions giving rise to films with optimal thickness for analysis. The reactions at 300−500 °C produced single-phase SnS_2 and can be idealized as shown in eq 1. The film grown at 525 °C yielded Sn_2S_3 and at 545 °C yielded SnS.

$$SnCl_4 + 2H_2S \rightarrow SnS_2 + 4HCl \qquad (1)$$

Compositional Analysis. The tin to sulfur ratio for each film was determined by EDX, XPS, and electron probe measurements. Electron probe measurements indicate compositions of $SnS_{1.96}$ (3 min deposition) and $SnS_{1.98}$ (30 s deposition) for samples produced at 300 °C. Maps of elemental composition for a 10 μm × 10 μm area (at ca. 0.1 μm elemental resolution) showed uniform tin to sulfur ratios for both samples prepared at 300 °C, with variations of less than two elemental percentage, in accord with EDX and XPS measurements. No chlorine or other elements were detected by these techniques. EDX (at 20 keV) of the material obtained at 300−450 °C did occasionally show some breakthrough of the excitation volume to the underlying glass. In that case silicon, calcium, sodium, and aluminum were also detected. The excitation volume on the EDX system used has a depth of ca. 1 μm, indicating that most of the films were on the order of 1 μm thick. This correlated with SEM measurements of the film thicknesses (typical growth rates of 1 μm min^{-1}). XPS did show some oxygen contamination on the surface of each film (between ca. 1−10 atom %; XPS interrogates the top ca. 10 atomic layers). Oxygen concentration decreased and tin and sulfur concentrations increased on argon etching during XPS depth profiling. This indicates that the oxygen is predominantly surface bound, a situation which probably comes about by handling and storage of the films in air and not via APCVD of a tin oxysulfide film. EDX measurements of films grown at temperatures between 350 and 495 °C showed slightly sulfur-rich films of composition $SnS_{2.04-2.20}$. Films grown above 500 °C showed significantly less sulfur; the film obtained at 525 °C had a tin to sulfur ratio of 1:1.6, corresponding most closely to Sn_2S_3, while the film grown at 545 °C had an elemental ratio of $SnS_{1.1}$. It is interesting to note that the Sn to S elemental ratios of single crystals of SnS_2 grown by vapor transport are slightly sulfur-rich, with a composition of $SnS_{2.02}$.[28]

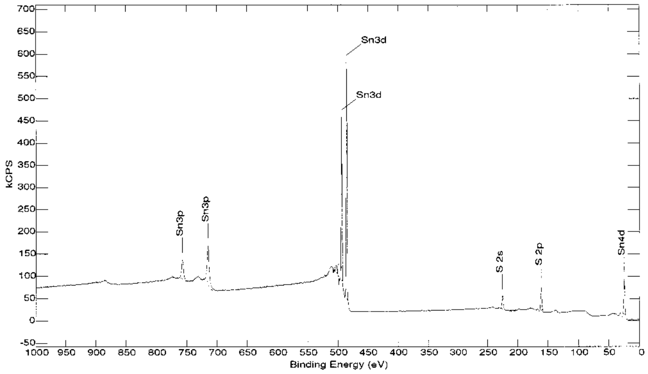

Figure 2. XPS spectrum of the film obtained from reaction of $SnCl_4$ and H_2S for 30 s at 300 °C.

The bulk XPS binding energy measurements for films grown from 300 to 495 °C gave a Sn $3d_{5/2}$ peak of 486.5 ± 0.1 eV and S $2p_{3/2}$ peak of 161.6 ± 0.2 eV dependent on the sample (Figure 2). These values agree with the two reported values[28] for SnS_2 of Sn $3d_{5/2}$ at 486.6 and 486.4 eV and S $2p_{3/2}$ peaks of 161.4 and 161.6 eV. Films grown at 545 °C had a Sn $3d_{5/2}$ peak at 485.7 eV and a S $2p_{3/2}$ peak of 161.0 eV. This compares extremely favorably with the Sn $3d_{5/2}$ peak reported for SnS of 485.6 eV.[29] Sulfur has a large range of binding energies: 161.7 eV in ZnS (S(−II)) to 171 eV in S(VI) compounds, with elemental sulfur appearing at 164.3 eV.[29] Binding energies observed for the tin sulfide films correspond to that observed for S in oxidation state −2. Notably only a single binding energy was observed for both S and Sn by XPS for all films, indicating that detectable levels of elemental Sn or S had not been incorporated into the films. This is particularly pertinent for the sulfur-rich films which had a sulfur to tin ratio of 2.20 (Table 1). The sulfur in excess of the SnS_2 stoichiometry is presumably bound to the tin and not present in elemental form. The binding energy for S in the SnS film is among the lowest recorded for sulfur.[29] The Sn binding energy for the Sn(IV) films is greater than that for the Sn(II) films by ca. 0.8 eV. These results agree with those found in other studies of tin halides and organometallic compounds for which the Sn(IV) compound has a peak at ca. 0.8−1.0 eV greater than that for the Sn(II) analogue.[29] Notably no chlorine was detected by XPS, even for films prepared at the lowest temperature (ca. 0.5 atom % detection limit). Previous work on the plasma-assisted CVD of $SnCl_4$ and H_2S showed the presence of tin sulfide films contaminated with up to 47 atom % chlorine.[25]

Film Color and Morphology. The color of the tin sulfide films changes with deposition temperature. At temperatures from 300 to 500 °C the films are yellow. However, longer reaction runs and higher H_2S flow rates produce black films at 300 °C (Table 1). The SEM micrographs show that at 300 °C the films have an ovoid appearance and dimensions of ca. 1000 nm × 500 nm for a film grown for 3 min, and a similar shape but smaller dimensions of 500 nm × 100 nm for one grown for 30 s (Figure 3a). The films that were laid down at higher temperatures (350−495 °C) are more platelike with dimensions of ca. 800 nm × 800 nm × 25 nm (Figure 3b). The film grown at 525 °C was brown with a yellow edge and consisted of a mixture of needlelike and wavy agglomerates (100 nm × 30 nm) (Figure 3c). The film produced at the highest temperature (545 °C) was gray and had a wavy agglomerated structure, as shown Figure 3d. The temperatures at which the films change color and morphology mirror the compositional

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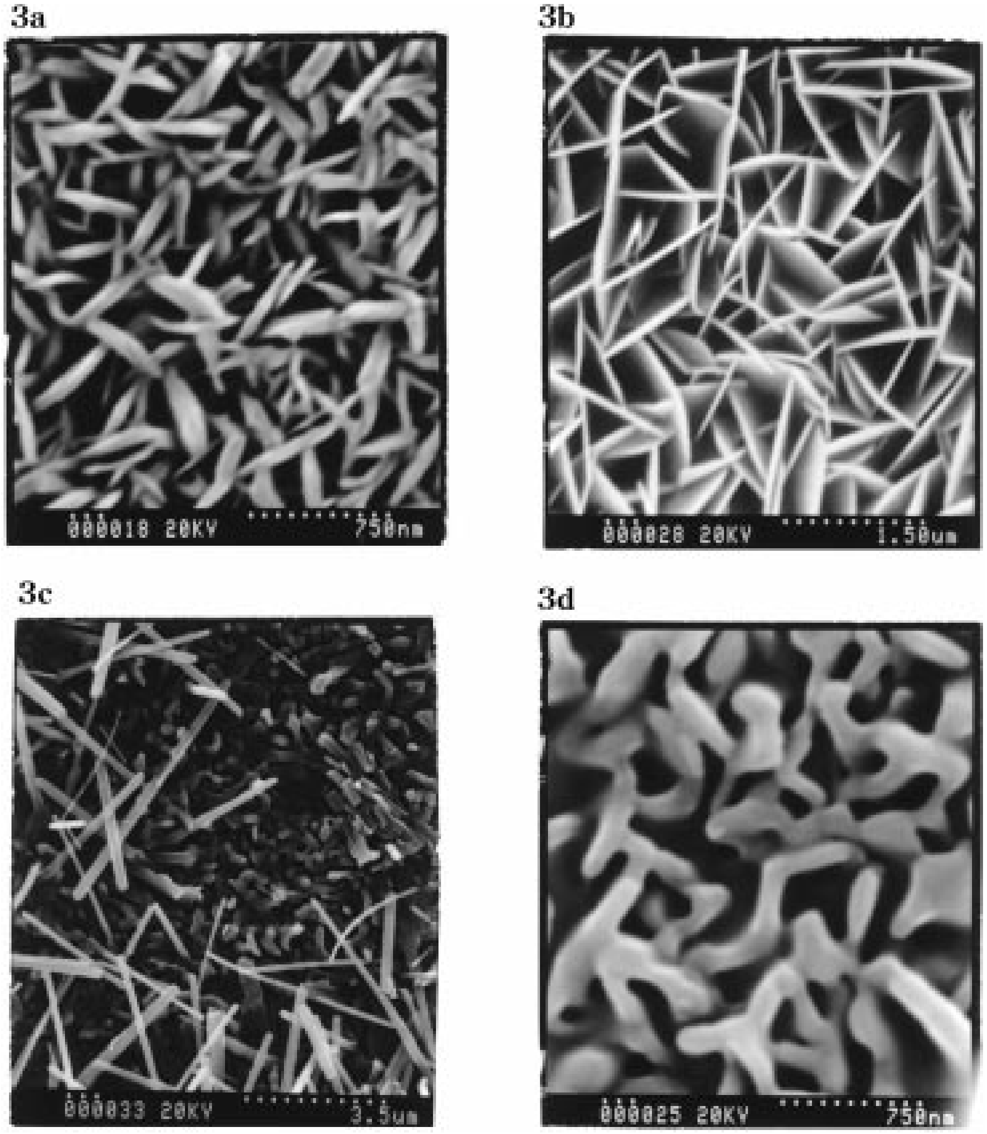

Figure 3. SEM micrographs of the films grown from the reactions of $SnCl_4$ and H_2S for 30 s at (a) 300 °C, (b) 475 °C, (c) 525 °C, and (d) 545 °C.

changes observed by EDX, XPS, and electron probe analysis. Both the SnS and SnS_2 films had the same crystal habits as found in previous bulk synthetic work.[1,16]

X-ray Powder Diffraction Studies. The glancing angle X-ray diffraction patterns for films grown at 300, 525, and 545 °C are shown in Figure 4a−c. These reveal that the low-temperature films (300−495 °C) consist of hexagonal SnS_2, the film grown at 525 °C consists of predominantly Sn_2S_3, and the film grown at 545 °C is due to orthorhombic SnS. The SnS_2 films grown at 495 °C gave cell parameters of $a = 3.65(1)$ Å and $c = 5.88(1)$ Å, which compare well to those from a TEM study ($a = 3.65$ Å and $c = 5.88$ Å) and from a number of X-ray reports[1,16,30] ($a = 3.62-3.65$ Å and $c = 5.85-5.90$ Å). The films grown at 300 °C for 3 min show some preferred orientation in the (100) direction. The film grown at 525 °C indexed as orthorhombic Sn_2S_3 ($a = 8.83(1)$ Å, $b = 3.76(1)$ Å, $c = 14.03(1)$ Å) (literature values $a = 8.80-8.84$ Å, $b = 3.75-3.77$ Å, and $c = 14.02$ Å[31]). The films grown at 525 °C also have three diffraction peaks at ca. 31°, 47°, and 51.5° that could not be accounted for on the basis of just Sn_2S_3 but are present in the diffraction pattern of SnS_2. This coating is thus a mixture of predominatly Sn_2S_3 with some SnS_2. Notably this film shows a Sn:S ratio of 1:1.60 by EDX. The film grown at 545 °C showed the X-ray diffraction pattern of single-phase orthorhombic SnS and could be indexed to $a = 4.32$ (1) Å, $b = 11.20$ (1) Å, and $c = 3.99$ (1) Å (literature values for SnS,[16,28] $a = 4.30-4.33$ Å, $b = 11.18-11.21$ Å, and $c = 3.98-4.02$ Å). It is worth pointing out that crystalline films were obtained at all temperatures and without recourse to annealing. Crystallite sizes of all the films were on the order of 250 Å from the Scherrer equation.

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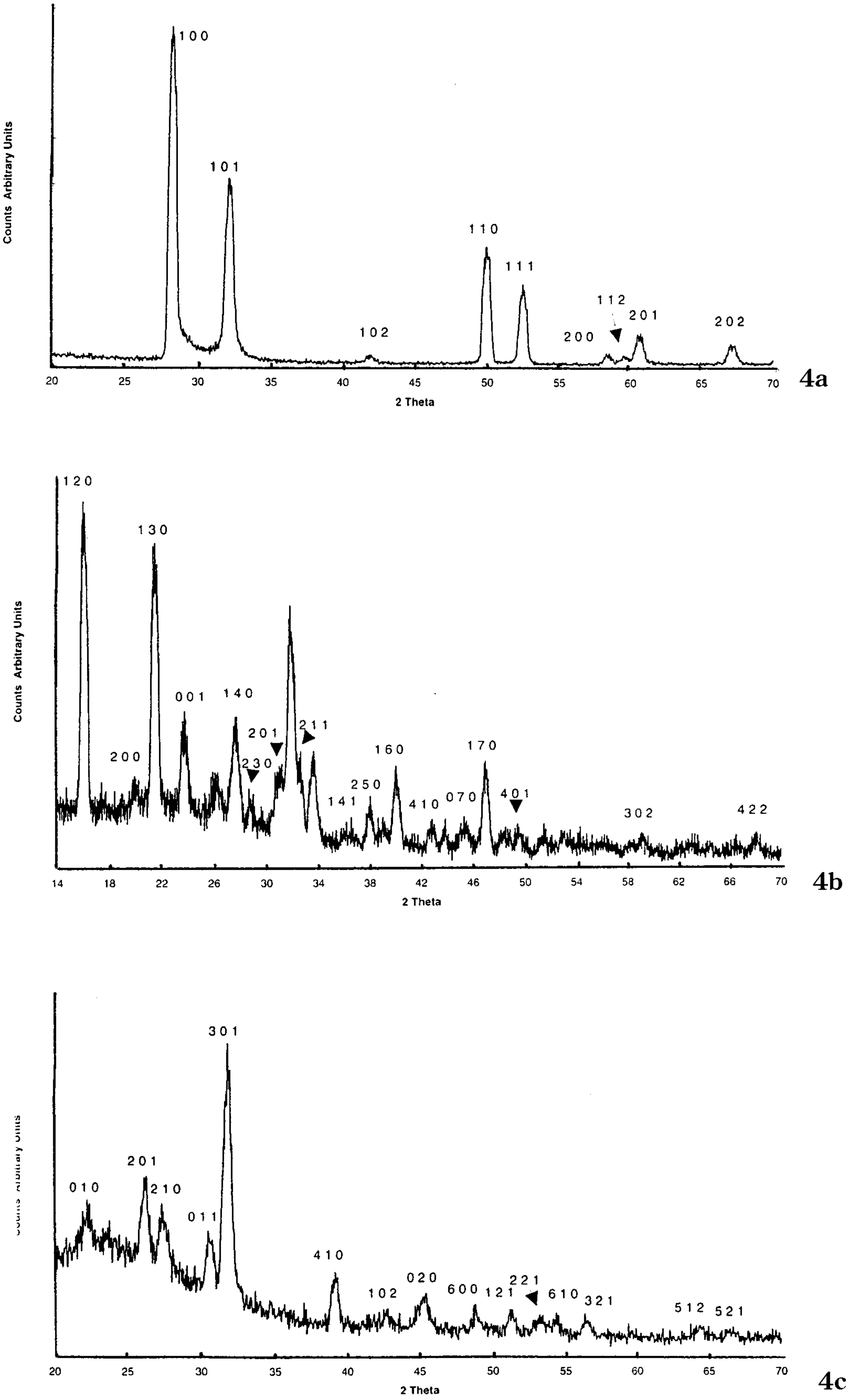

Figure 4. X-ray diffraction patterns for the films grown from the APCVD reaction of H_2S and $SnCl_4$ at (a) 300 °C, (b) 525 °C, and (c) 545 °C. Indexed peaks at 300 °C for SnS_2, at 525 °C for Sn_2S_3, and at 545 °C for SnS. 2θ values are in degrees.

Raman Studies. The Raman spectra of the yellow films grown at 300–500 °C show two bands at 312 and 215 cm^{-1} (Figure 5a). These match most closely with the reported spectra of single-crystal SnS_2 of the 2H polytype structure (317 and 209 cm^{-1}).[32] The intense band at 312 cm^{-1} has been assigned to the A symmetry intralayer mode and the band around 215 cm^{-1} to an E mode.[32] Notably the reported single-crystal Raman

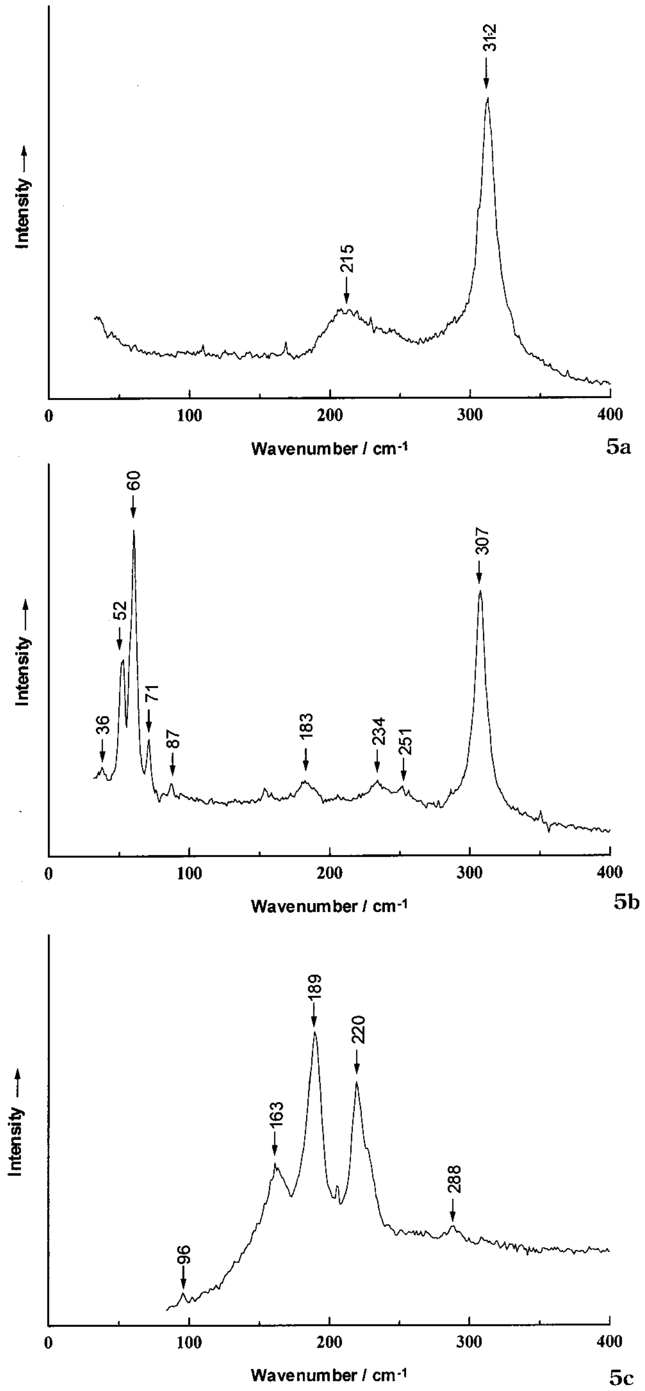

Figure 5. Raman spectra of (a) the film obtained at 300 °C (corresponding to SnS_2), (b) the film obtained at 525 °C (corresponding to Sn_2S_3), and (c) the film obtained at 545 °C (corresponding to SnS). Spectra 5a and 5b were measured on the Dilor XY spectrometer and spectrum 5c with the Renishaw spectrometer.

spectra of the polytypes 4H SnS_2 and 18R SnS_2 show three distinct bands from 216 to 198 cm^{-1}. In the present work it was noted that the intensity of the band at 215 cm^{-1} is a function of laser orientation. Raman analysis of a commercial bulk amorphous sample of SnS_2 showed an intense band at 314 cm^{-1} and a weaker one at 220 cm^{-1}. The film grown at 525 °C showed bands at 307, 251, 234, 183, 71, 60, and 52 cm^{-1} (Figure 5b). This corresponds to the Raman reference spectrum for Sn_2S_3.[33] The intensities of the various Raman bands for Sn_2S_3 have been reported as a function of crystal orientation. Interestingly, the relative intensities of the Raman bands of Sn_2S_3 on glass in these experiments correspond exactly to the spectrum reported for the (*yy*) polarization.[33] This indicates that the Sn_2S_3 crystallites are laid down with preferred orientation on the surface. The silver-colored film grown at 545 °C showed a very different Raman pattern (Figure 5c), with bands at 288, 220, 189, 163, and 96 cm^{-1}. This pattern corresponds exactly to that given by a single crystal of SnS with a random orientation of crystallites on the glass.[34]

Film Properties. The tin sulfide coatings were fairly adherent to the glass substrate, passing the Scotch tape test, but could be wiped off by vigorous rubbing. The coatings were in most cases uniform across the whole glass surface (225 mm × 89 mm). However, the brown film grown at 525 °C did show some yellow coloration at the edges. The tin sulfide films did not change in color or composition on storage in air. During the APCVD runs very little blockage occurred in the mixing tube where the gas streams met. The mixing tube was at a temperature of ca. 150 °C; indeed, prereaction is unlikely at this temperature, as no films could be grown for this system below 200 °C. Previous APCVD runs on experiments aimed at forming metal nitrides from ammonia and metal halides were frequently blocked by products formed in the mixing chamber prior to entering the coater; this led to some contamination of the films by particulates. Such behavior was not observed for the formation of tin sulfide films. The latter were shown to be poor electrical conductors by sheet resistance measurements. UV measurements for films grown between 300 and 500 °C showed a direct band gap of 2.14 eV, equivalent to that reported for SnS_2 (2.1−2.3 eV).[1,5] It was noted that, for the 3 min run at 300 °C, some deposition of SnS_2 occurred on the “cold” quartz walls of the CVD reactor as well as on the top plate of the reactor. This film was black in color, nonadherrant, and could be removed by Scotch tape; moreover, it was crystalline and gave an X-ray powder diffraction pattern for SnS_2.

Discussion

The APCVD reaction of $SnCl_4$ and H_2S gives fast growth rates of good-quality, crystalline tin sulfide films. At all temperatures an excess of H_2S is present in the system. At temperatures from 300 to 495 °C, SnS_2 films are produced; at 525 °C, Sn_2S_3 is produced; and at 545 °C, SnS films are favored. Thus the sulfur content of the films decreases with deposition temperature. The reason for this changeover in film composition is not entirely clear, as both SnS and SnS_2 have decomposition points above 800 °C. Thus it is unlikely that the SnS and Sn_2S_3 are obtained by thermal decomposition of SnS_2. Previously we have reported the formation of mixtures of SnS and SnS_2 from the bulk elemental reaction of tin and sulfur in liquid ammonia.[15] Thermolysis of this mixture under vacuum conditions pro-

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duces, at 400 °C, single-phase SnS. This reaction was assisted in part by the presence of some tin metal which was considered to undergo a comproportionation reaction with SnS_2 to form SnS. The remainder of the SnS_2 evolved some sulfur under high vacuum conditions to form SnS. In the current CVD experiments, the depositions were carried out at atmospheric pressure and for a relatively short duration; thus, it is likely that Sn_2S_3 and SnS films are kinetic products in the reaction at high temperature and not formed from decomposition of the SnS_2 films. Notably previous approaches to tin sulfides using either Sn(IV) or Sn(II) precursors at 480 °C always gave SnS with no detectable SnS_2 products.[16,30] Single crystals of SnS_2 can be grown from the elements by vapor transport at temperatures in excess of 670 °C.

To our knowledge there have been two previous reports of forming tin sulfide coatings by CVD, and in both cases only SnS films were obtained. The reaction of $SnCl_4$ and H_2S in a hydrogen atmosphere at 150−200 °C using plasma-assisted CVD on small silica substrates (1 cm × 2 cm) was reported to yield relatively impure SnS coatings.[9] At low plasma levels, significant chlorine contamination of the films was observed. At higher plasma levels and temperatures, crystalline films were observed that contained some SnS. X-ray fluorescence analysis gave a film composition at nearest to SnS of $SnS_{0.80}$, while the X-ray diffraction patterns showed mixed phases with some SnS which had preferred growth along the (111) planes. The second report was on the OMVPE deposition of tin sulfide coatings on CaF_2 and MgF_2 substrates from the reactions of either tetramethyltin or tetraethyltin with hydrogen sulfide at 500−625 °C.[31] The authors did not report any characterization data on the films except for the film thickness (3 μm). The tin sulfide films were yellow or gray (thus matching what we observed in these experiments) and were thought to be of SnS because they had been grown in a reducing hydrogen atmosphere.

The exact substrate temperature for the APCVD reaction of $SnCl_4$ and H_2S affects the nature of the films produced. This is particularly important for the temperature window between 500 and 545 °C. The Raman microscopy study enabled specific areas of the same samples to be investigated. The film which was grown at 525 °C was predominantly brown but with yellow edges; the latter comprised predominantly Sn_2S_3 but also contained a trace of SnS_2 by XRD measurements (4 cm × 4 cm area analyzed, including the edge of the film). Raman microscopy on the same sample traced the presence of SnS_2 exculsively to the yellow edges of the coating and of Sn_2S_3 to the central brown portion. This observation can be correlated with the small variance of temperature across the glass substrate during deposition. The results correlate well with the observed elemental percentages from EDX and electron probe measurements in which the large area study of the film grown at 525 °C showed a sulfur to tin ratio of 1.60. The Raman microscopy study also indicates the presence of some small regions of Sn_2S_3 on the edges of the SnS film grown at 545 °C, this result correlating with the observed XPS sulfur to tin ratio of 1.10. Thermocouple measurements on the glass during deposition indicate that the edges are ca. 5−10 °C cooler than the center, this small variation probably accounting for the observed phases on the “colder” edges of the glass.

The relatively poor adherence of tin sulfide on glass substrates may limit the application of these films. One method that could improve adherence would be to apply an undercoat of a material of similar crystal structure to the glass before coating with tin sulfide. We are currently studying the incorporation of APCVD-prepared tin sulfide films into photovoltaic devices.

Conclusions

Tin sulfide films can be grown by APCVD reaction of tin(IV) chloride and H_2S. At deposition temperatures from 300 to 500 °C yellow SnS_2 was obtained; at 525 °C, Sn_2S_3 was obtained; while at 545 °C, a single-phase gray SnS film was formed. The APCVD reaction of $SnCl_4$ and H_2S provides a rapid route for the formation of good-quality, chlorine-free tin sulfide coatings. The tin sulfide films are air stable, fairly adhesive, and under APCVD conditions give good growth rates (ca. 1 $\mu m\ min^{-1}$). The APCVD tin sulfide films show virtually identical charateristics (XPS, XRD, morphology, band gap) to authentic bulk materials.

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