

Growth of thin layers of metal sulfides by chemical vapour deposition using dual source and single source precursors: routes to Cr₂S₃, α-MnS and FeS†

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The growth of thin layers of the transition metal sulfides Cr₂S₃, α-MnS and FeS by Chemical Vapour Deposition (CVD) is reported. Layers of Cr₂S₃ in the rhombohedral or trigonal form have been grown onto Pyrex, molybdenum or aluminium substrates using the single-source precursor Cr(S₂CN(C₂H₅)₂)₃ in a low-pressure flow reactor. The temperature of the precursor was held at 255 °C and the substrate was heated to 450 °C for these experiments. The nature of the layer formed was determined by a combination of EDX analysis and glancing angle XRD. Growth rates up to 10 μm h⁻¹ were achieved. In a separate series of experiments thin layers of α-MnS and FeS have been grown onto Pyrex substrates using propylene sulfide (C₃H₆S) as the sulfur source and CpMn(CO)₃ (Cp = η-C₅H₅) or Cp₂Fe as the metal source using a CVD reactor under a flow of nitrogen gas. An approximately 1 : 1 molar ratio of C₃H₆S and CpMn(CO)₃ and a substrate temperature of 410 °C gave a growth rate of α-MnS of some 4 μm h⁻¹ and a crystalline layer as shown by EDX analysis and powder XRD. However, increasing the flow rate of the sulfur source or decreasing that of the metal source gave rise to sulfur-rich layers. Layers of FeS were grown on Pyrex substrates from C₃H₆S and Cp₂Fe with a molar ratio of reactants of 1 : 3 or higher and a substrate temperature of 410 °C. A growth rate of around 2.5 μm h⁻¹ was achieved.

Introduction

There is currently much interest in the growth of thin layers of metal chalcogenides, including metal sulfides, by Chemical Vapour Deposition (CVD). In part this interest results from the known property of several of these compounds as photoconductors¹ although a detailed, systematic survey has not been carried out. An example of the potential use of compounds of this type is that of MoSe₂ and WSe₂ in the conversion of solar energy to electrical power.

Various experimental techniques have been employed in the growth of thin films of metal chalcogenides including sputtering, plasma CVD, chemical bath deposition and CVD. The last of these methods has, however, so far not attracted much attention. Hofmann *et al.*² investigated the production of thin films of MoS₂, WS₂ and Mo_xW_(1-x)S₂ using the hexacarbonyls Mo(CO)₆ or W(CO)₆ as the metal source and H₂S as the sulfur source. A potential problem of H₂S as a precursor is that of prereaction.^{3,4} In earlier work we have shown that prereaction in the formation of layers of CdS may be conveniently avoided by replacing H₂S with propylene sulfide (C₃H₆S) as the sulfur source.^{5,6} Another way to avoid prereaction is to move to a single source precursor. There have, however, been very few examples of the use of single source precursors in the production of a transition metal sulfide layer: one example is the use of Mo(SBu)₄ in the formation of highly pure layers of MoS₂.⁷ Accordingly we present here a two-part study. In the first part we have employed the dithiocarbamate

complex Cr(S₂CN(C₂H₅)₂)₃ to grow thin layers of Cr₂S₃. In the second part we have used propylene sulfide in dual source experiments to grow layers of MnS, using CpMn(CO)₃ {Cp = η-C₅H₅} as the metal source, and of sulfur deficient FeS, using Cp₂Fe as the metal source.

There are many examples of dithiocarbamates being used as single source precursors for thin film growth. The majority of these concentrate on the production of lead, cadmium, zinc, copper and indium sulfides from a variety of dithiocarbamates. These layers all exhibit semiconducting properties and are important optoelectronic materials. The types of compounds used are normally relatively simple compounds, such as Pb(S₂CNBuⁿ)₂⁸ and M(S₂CN(C₂H₅)₂)₂ (M = Pb, Cd)⁹ in the production of lead and cadmium sulfides respectively. Similarly, Zn(S₂CN(C₂H₅)₂)₂ has been used in the production of zinc sulfide.^{10,11} In summary, the sulfides of these metals are good photovoltaic materials and the metal dithiocarbamates have been found to be useful precursors, replacing the use of hazardous metal alkyls and poisonous hydrides. High quality crystalline materials have been reported as products from the thermal decomposition of metal dithiocarbamates and related compounds such as thiocarboxylates¹² and dialkyldiselenocarbamates.¹³

The use of copper and indium dithiocarbamates as single source precursors has also been reported with one and both metals as part of the precursor. For example, In₂S₃ films have been obtained from the decomposition from BuⁿIn(SPrⁱ)₂¹⁴ and Cu₂S formed from Cu(S₂CNPr₂)₂ while copper–indium binuclear precursors such as Bu₂In[S(Prⁱ)]Cu(S₂CNBu₂)₂¹⁵ and other related compounds with different alkyl groups¹⁶ have been shown to give crystalline CuInS₂ layers of high purity.

In order to extend these studies the reactions between the metal sources CpMn(CO)₃ and Cp₂Fe and the sulfur source propylene sulfide C₃H₆S have been investigated. Propylene sulfide was selected as the sulfur source as this had been used

†Throughout this paper the formula FeS is used to denote a binary material with a range of stoichiometries from 44–53% Fe. This finding is not unexpected given the typically non-stoichiometric nature of FeS. See, for example, F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, *Advanced Inorganic Chemistry*, 6th edn., Wiley-Interscience, New York, 1999, p. 508.

successfully in previous experiments to generate layers of CdS in dual source experiments where Me_2Cd was used as the Cd source.^{5,6} $\text{CpMn}(\text{CO})_3$ has previously been used as a metal source in the formation of (Hg,Mn)Te alloys,¹⁷ while $\text{MeMn}(\text{CO})_5$ has been employed in the production of alloys containing mercury, manganese, cadmium and tellurium.^{18,19} Previous work concerning the formation of pyrite (FeS_2) by CVD has centred on the use of $\text{Fe}(\text{CO})_5$ as the iron source with di-*tert*-butyldisulfide or propylene sulfide as the sulfur source.^{20a} In the current work, while maintaining propylene sulfide as one of the precursors we have selected ferrocene Cp_2Fe as the metal source. In part this choice results from the greater ease of handling and lower toxicity of Cp_2Fe over $\text{Fe}(\text{CO})_5$ which make it potentially more suitable as a precursor for CVD. In this context it may be noted that iron(III) acetylacetonate has been used in a very recent experiment with di-*tert*-butyldisulfide in an H_2 flow to grow thin layers of FeS_2 .^{20b}

Experimental

Infrared spectra of solids were recorded on a Perkin-Elmer FTIR spectrometer (1720-X) with a resolution of $\pm 1 \text{ cm}^{-1}$. Gas phase FT-IR measurements were on samples contained in an evacuated gas cell (path length *ca.* 10 cm) fitted with CsI windows and sealed with a Young's Tap. Thermal Gravimetric analyses were determined using a Stanton Redcroft STA 1000 Simultaneous Thermal Analyser designed to give thermogravimetric analysis (TGA) and differential thermal analysis (DTA) simultaneously. All samples were referenced to recalculated alumina. The thermal analyses were run at a heating rate of $10^\circ\text{C min}^{-1}$ in a flow of nitrogen. A JEOL JXA-840 Scanning EDXA Microanalyser attached to the Scanning Electron Microscope (SEM) was used to obtain elemental analysis of layers grown; the SEM was also used to study the morphology of the layers grown. Powder X-Ray diffraction was performed using a Siemens/Brucker AXS D5000, monochromated dual goniometer diffractometer.

A sample of $\text{Cr}(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_3$ was prepared and characterised as described elsewhere.²¹⁻²³ All other reagents were purchased from Aldrich and used as supplied.

Apparatus used for the growth experiments

Experiments were carried out in which precursors were heated under vacuum in a static system, under dynamic vacuum, or in a flow of N_2 gas. For static systems $\text{Cr}(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_3$ (0.02 g, 0.04 mmol) was sealed into separate Pyrex vessels, each with a volume of *ca.* 150 cm^3 . A microscope cover slip was sealed into each reaction vessel with the sample, to provide a flat surface which was later used in the analysis of the solid decomposition product by SEM and XRD. The vessel was placed into an oven and was held at a temperature of 450°C for 18 h. The vessel was allowed to cool to room temperature, *ca.* 25°C , and gaseous products were analysed by FT-IR. In separate experiments, the decomposition of $\text{CpMn}(\text{CO})_3$ or of Cp_2Fe in the presence of propylene sulfide was studied. In these cases a 1 : 1 molar ratio of the precursors was placed into the reaction vessel which was sealed *in vacuo*. The experiment was then carried out as above.

A horizontal cold-walled CVD reactor was constructed in Reading specifically for studying CVD growth of thin layers from single- and dual-source precursors. The reactor, as set up for a dual-source experiment, is illustrated in Fig. 1. It was possible to connect the reactor to a vacuum line. The reactor consisted of a quartz tube, of length 50 cm and diameter 5 cm, with a small tapered inlet at one end. At the opposite end, the internal heating system was connected to an external power supply and controller *via* four tungsten rods, sealed into the quartz socket. The heating system consists of a cartridge heater

and a thermocouple. The heat is supplied to a graphite block inside the reactor. To assist in maintaining the elevated temperature of the graphite block a small tube furnace was placed around the reactor, at the position of the block, to provide additional heating and to act as insulation.

For single-source precursor experiments the following procedure was adopted. A sample of the precursor $\text{Cr}(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_3$ (*ca.* 50 mg) was placed into a small sample boat (dimensions: $1 \text{ cm} \times 4 \text{ cm} \times 0.5 \text{ cm}$) made of Pyrex. The boat was placed into a quartz adaptor, which fitted onto the inlet end of the reactor. The sample was heated using a small tube furnace connected to a thermocouple and a temperature controller. This furnace was placed around the tube and adjoining the furnace which surrounds the graphite block. This arrangement eliminates cold spots in the tubing between the vaporised sample and hot substrate so that no condensation occurs which could block the inlet to the reactor. A quartz stopper was used to seal the adaptor so that the reaction could be carried out under vacuum.

A number of substrate materials were used, these included Pyrex microscope slides supplied by BDH. Molybdenum foil (0.5 mm, 99.9%) thick, and aluminium foil (1.0 mm, 99.99%) cut into 1.5 cm^2 , supplied by Aldrich, were also used. For dual-source precursor experiments this procedure was modified slightly as shown in Fig. 1. Here the solid precursor $\text{CpMn}(\text{CO})_3$ or Cp_2Fe (*ca.* 50 mg) was placed into the sample boat while the liquid propylene sulfide (*ca.* 5 cm^3) was placed into the Pyrex bubbler held inside a slush bath. Nitrogen gas was used to transport the precursors over the heated substrate. The flow rate for N_2 was monitored using a direct reading flow meter (Gilmont Flowmeter, flow range $20\text{--}2100 \text{ cm}^3 \text{ min}^{-1}$, $\pm 5\%$). The total flow rate of N_2 and propylene sulfide was monitored using a burette flow meter, attached by rubber tubing to the outlet of the reactor. The flow rate of the propylene sulfide could be calculated by subtraction of the reading from the flow meter from the total rate measured with the burette. The "actual" flow rate of the metal source was calculated by multiplying the partial pressure of the reagent (at the temperature at which the reagent was held) by the flow rate of nitrogen.²⁴

Results and discussion

Decomposition under static conditions

Gaseous products from the decomposition of $\text{Cr}(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_3$ in a static reactor held at 450°C for 18 h were analysed by FT-IR. The gaseous products identified were CH_4 , C_2H_4 , CS_2 and HCN .²⁵⁻²⁷ These results correlate well with results from previously published decomposition studies concerning dithiocarbamate compounds.²⁸⁻³⁰ A dark green solid was found to be adhering to the glass slide within the static reactor at the end of the experiment. This was analysed by EDX, which showed the elemental composition to be Cr_2S_3 , and by powder XRD. In a separate series of experiments 1 : 1 molar mixtures of $\text{CpMn}(\text{CO})_3$ (160 mg) and propylene sulfide (60 mg) or Cp_2Fe (150 mg) and propylene sulfide (60 mg) were heated to 450°C for periods between 3 and 18 h in a static reactor. Gaseous products were investigated by a combination of FT-IR spectroscopy and mass spectrometry. In the $\text{CpMn}(\text{CO})_3$ experiment the gaseous products positively identified were CO, propene and methane;²⁵⁻²⁷ the Cp_2Fe experiment yielded propene and methane only.²⁵⁻²⁷ These products are expected although it is not clear as to the exact fate of the coordinated $\eta\text{-C}_5\text{H}_5$ group. There is no sign of any hydrocarbon larger than propene; in particular the mass spectrum shows no peak with an m/z value greater than 42. From each of these experiments a solid was recovered which adhered to the glass slide in the reactor. For the $\text{CpMn}(\text{CO})_3$ experiment a combination of EDX and powder X-ray

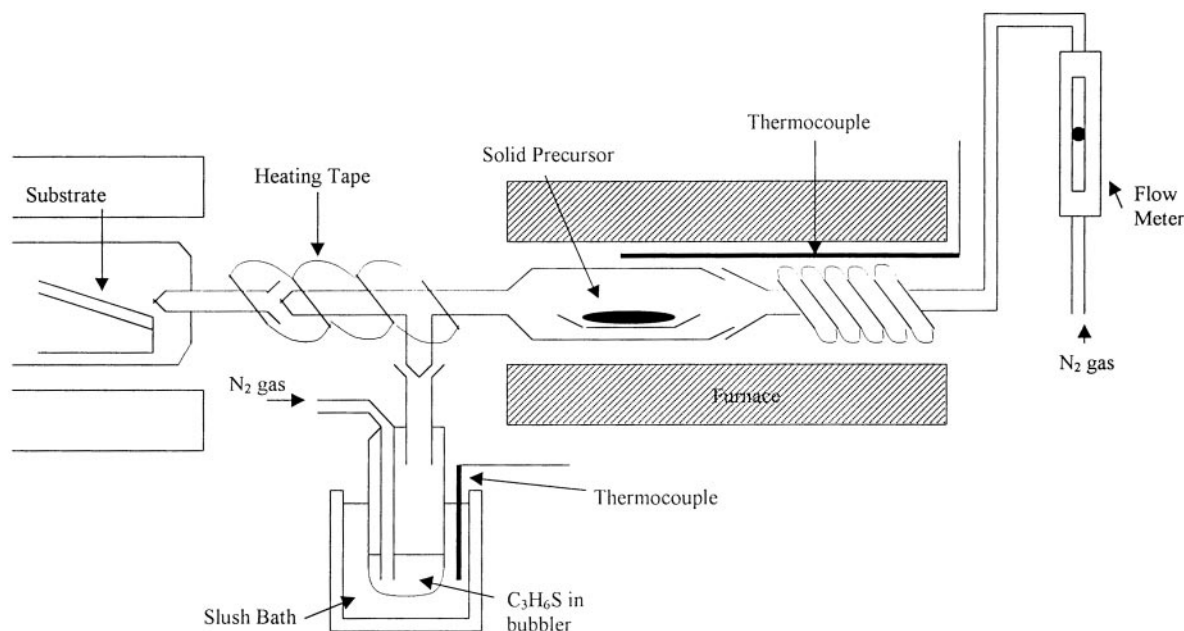


Fig. 1 Schematic diagram of flow reactor as set up for use with dual-source precursor experiments.

diffraction shows this to be highly crystalline α -MnS.³¹ For the Cp₂Fe experiment the product is identified as a crystalline sample of FeS.³²

Thermal decomposition of Cr(S₂CN(C₂H₅)₂)₃ was also carried out under a nitrogen flow and was monitored by Thermal Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) as the sample was heated at a rate of 10 °C min⁻¹. The TGA and DTA traces are illustrated in Fig. 2. The sample is seen to melt at 255 °C and to decompose between 350 °C and 375 °C, after which no further change in mass was observed. The final mass recorded corresponds to the formation of Cr₂S₃. An accompanying exothermic enthalpy change is also seen.

Growth experiments under flow conditions

In an attempt to mimic more closely a CVD reactor, and to grow thin layers of a sulfide product, the decomposition of Cr(S₂CN(C₂H₅)₂)₃ was studied under 'flow' conditions using the apparatus described in detail earlier in this paper. A sample of Cr(S₂CN(C₂H₅)₂)₃ (60 mg) was placed into the sample boat and the reactor sealed. Air was then evacuated from the reactor, and the Pyrex substrate heated to 450 °C using the graphite block. The sample was then slowly heated to 255 °C, and maintained at this temperature, under reduced pressure, for 0.5 h; these sample and substrate temperatures were selected following inspection of the TGA/DTA traces for the sample. The vaporised sample was passed over the heated substrate using the vacuum line pumping system. On examination of the substrate, a dark layer was found to have formed on the substrate, around the sample inlet.

Films deposited were found to be of uniform morphology and to consist of closely packed crystals of Cr₂S₃. Analysis of

the surface using EDX analysis showed uniformity in the elemental composition of the film. The thickness of the Cr₂S₃ layer grown onto Pyrex was determined by scoring the underside of the slide to achieve a clean break along the slide. The slide was then covered in a thin film of gold in order to enable conduction of the glass surface, and so eliminate 'charging' effects. This enabled good quality photographs (see Fig. 3) to be obtained of the cross-section of the layer. The layer was found to be 5 μm at its thickest point, giving a maximum growth rate of 10 μm h⁻¹.

The amorphous nature of the Pyrex substrate was found to yield layers which were unsuitable for study by X-Ray Diffraction. Thus a layer grown onto molybdenum foil was used for glancing angle XRD. The results obtained show, alongside a large Mo (110) peak due to the substrate material, peaks identified as arising from highly crystalline, rhombohedral Cr₂S₃.³² The XRD pattern, indexed according to the rhombohedral form, is illustrated in Fig. 4. It should be noted

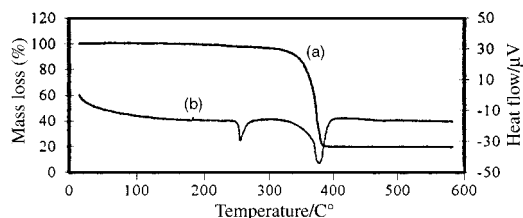


Fig. 2 TGA (a) and DTA (b) traces for the decomposition of Cr(S₂CN(C₂H₅)₂)₃ under N₂.

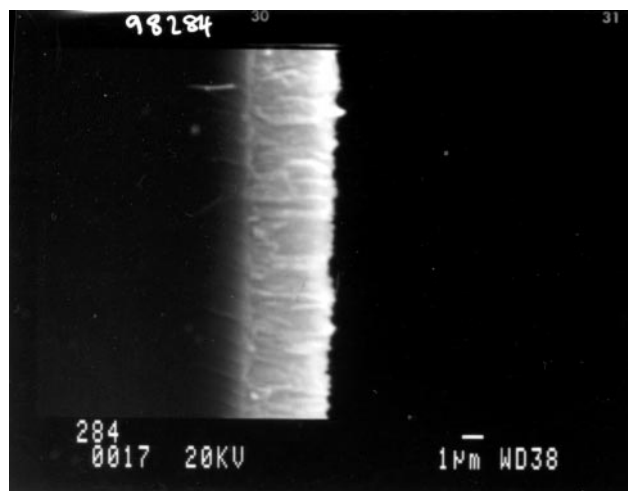


Fig. 3 Scanning Electron Micrograph of a cross-section of a layer of Cr₂S₃ grown onto a Pyrex substrate. For this experiment the Cr(S₂CN(C₂H₅)₂)₃ precursor was held at a temperature of 255 °C and the substrate at 450 °C. The elemental composition of this layer as measured by EDXA is Cr 40.38%, S 59.62%. The growth has been performed for 0.5 h and the thickness of the layer is seen to be ca. 5 μm. The slide has been coated in a thin film of gold in order to enable conduction of the glass surface and to eliminate "charging" effects.

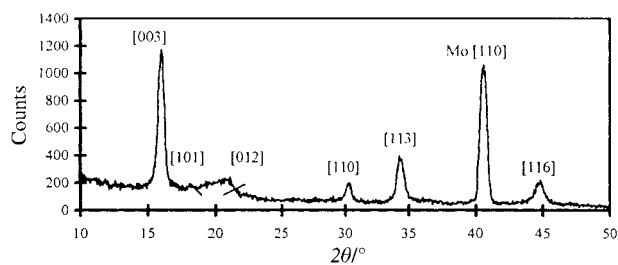


Fig. 4 The XRD pattern of a thin layer of Cr_2S_3 grown onto a Mo foil substrate obtained by glancing angle methods. The XRD trace has been indexed according to the rhombohedral form of Cr_2S_3 .

that the glancing angle technique employed disrupts intensity values for these features, so that the intensities of the peaks are not directly comparable with those in the literature. Moreover, the trigonal form of Cr_2S_3 gives a very similar diffraction pattern to that given by the rhombohedral form.^{33,34} It is, of course, possible that a mixture of the two forms is present.³⁵ A photograph of a thin layer of Cr_2S_3 grown on a Mo substrate and obtained using the SEM is given in Fig. 5. The layer is seen to consist of closely-packed crystals superimposed onto the ridged surface of the metal.

An attempt to grow thin layers of MnS was made using $\text{CpMn}(\text{CO})_3$ and $\text{C}_3\text{H}_6\text{S}$ as precursors using the flow apparatus as described in detail earlier in this paper. A Pyrex substrate was employed. It was found that the exact conditions under which the experiment was performed were critical. A substrate temperature of 410°C , together with a slight excess of the sulfur-containing precursor (*ca.* 1.2:1), was found to be optimum. To achieve these conditions the $\text{CpMn}(\text{CO})_3$ sample was held at 60°C and the propylene sulfide sample at -40°C . The flow rates were: $\text{CpMn}(\text{CO})_3=0.14$ and $\text{C}_3\text{H}_6\text{S}=0.17\text{ cm}^3\text{ min}^{-1}$. At higher $\text{C}_3\text{H}_6\text{S}$ flow rates (2.5 to $6.5\text{ cm}^3\text{ min}^{-1}$), lower $\text{CpMn}(\text{CO})_3$ flow rates ($0.06\text{ cm}^3\text{ min}^{-1}$) or when quartz substrates were used in place of Pyrex, sulfur-rich layers of manganese sulfide were formed. By contrast, at very low $\text{C}_3\text{H}_6\text{S}$ flow rates ($0.03\text{ cm}^3\text{ min}^{-1}$) or at higher substrate temperatures (425°C), manganese-rich layers were formed. Under optimum conditions a 1:1 molar ratio of Mn:S was seen by EDXA in the layer; the surface morphology of such a layer is illustrated in the micrograph given in Fig. 6. It is seen to consist of small granular particles. A small sample was removed from this layer and analysed by powder XRD. This

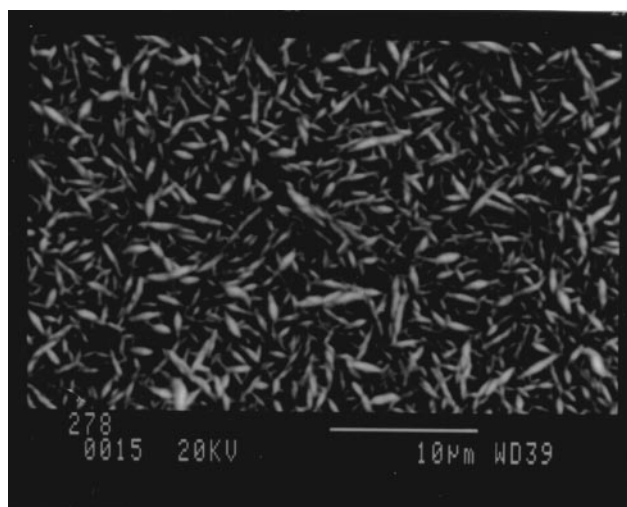


Fig. 5 Scanning Electron Micrograph of a thin (*ca.* $1\text{ }\mu\text{m}$) layer of Cr_2S_3 grown onto a Mo foil substrate. For this experiment the $\text{Cr}(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_3$ precursor was held at a temperature of 255°C and the substrate at 450°C . The elemental composition of this layer as measured by EDXA is Cr 40.38%, S 59.62%.

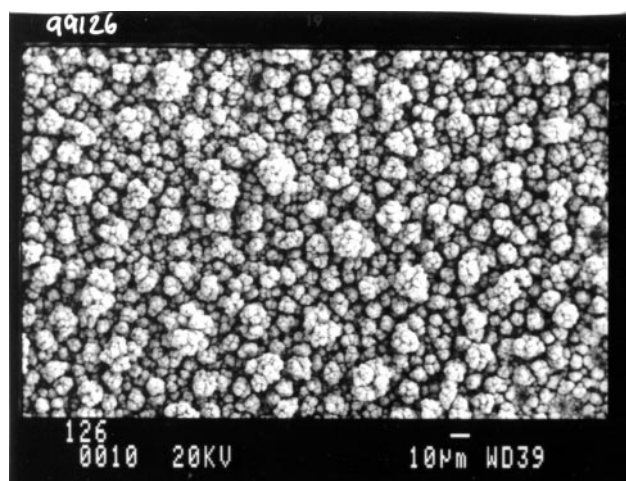


Fig. 6 Scanning Electron Micrograph of a thin (*ca.* $1\text{ }\mu\text{m}$) layer of MnS grown onto a Pyrex substrate using $\text{CpMn}(\text{CO})_3$ and $\text{C}_3\text{H}_6\text{S}$ as precursors. The conditions employed were: $\text{CpMn}(\text{CO})_3$, temperature 60°C , flow rate $0.14\text{ cm}^3\text{ min}^{-1}$; $\text{C}_3\text{H}_6\text{S}$, temperature -40°C , flow rate $0.17\text{ cm}^3\text{ min}^{-1}$; substrate temperature 408°C . The elemental composition of this layer as measured by EDXA is Mn 48.95%, S 51.05%.

confirms that the layer is $\alpha\text{-MnS}$.³⁴ When the flow rates were set at $\text{CpMn}(\text{CO})_3=0.14$ and $\text{C}_3\text{H}_6\text{S}=0.17\text{ cm}^3\text{ min}^{-1}$ the growth layer of the $\alpha\text{-MnS}$ layer was found to be *ca.* $4.0\text{ }\mu\text{m h}^{-1}$.

FeS layers were grown similarly by CVD using Cp_2Fe and $\text{C}_3\text{H}_6\text{S}$ as precursors. In the growth of $\alpha\text{-MnS}$ the highest quality layers were formed when the temperature of propylene sulfide was maintained at -40°C and the substrate at 410°C . These conditions were used for the reactions between ferrocene and propylene sulfide. The Cp_2Fe was heated at temperatures between 125 and 175°C thus giving a large excess of the iron source (3–30 fold). These conditions gave reproducible crystalline layers of FeS as shown by EDXA. The surface morphology of a typical layer is shown in Fig. 7. A small sample of the solid material forming this layer was removed from the substrate and was studied by powder XRD. This identified the sample as FeS.³⁵ A typical growth rate for FeS layers grown under these conditions with flow rates of $\text{Cp}_2\text{Fe}=0.34\text{ cm}^3\text{ min}^{-1}$ and $\text{C}_3\text{H}_6\text{S}=0.11\text{ cm}^3\text{ min}^{-1}$ was found to be *ca.* $2.5\text{ }\mu\text{m h}^{-1}$.

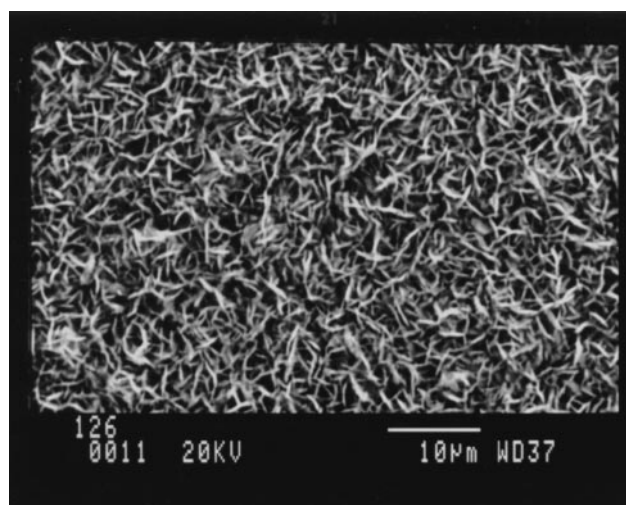


Fig. 7 Scanning Electron Micrograph of a thin (*ca.* $1\text{ }\mu\text{m}$) layer of FeS grown onto a Pyrex substrate using Cp_2Fe and $\text{C}_3\text{H}_6\text{S}$ as precursors. The conditions employed were: Cp_2Fe , temperature 175°C , flow rate $2.97\text{ cm}^3\text{ min}^{-1}$; $\text{C}_3\text{H}_6\text{S}$, temperature -40°C , flow rate $0.11\text{ cm}^3\text{ min}^{-1}$; substrate temperature 412°C . The elemental composition of this layer as measured by EDXA is Fe 54.13%, S 45.87%.

Experiments carried out using a molybdenum substrate to attempt to grow layers of either MnS or of FeS proved unsuccessful as all that was formed was a layer of the sulfide of the metal substrate. This led to difficulties in obtaining XRD patterns of the layers. Repeated attempts at obtaining a pattern of the layers grown onto glass or quartz using the glancing angle diffraction technique were unsuccessful. This was due to the thinness of the samples (1–2 μm) which allowed the X-ray beam to pass through the samples and consequently the trace consisted of a large broad peak due to the glass substrate that obscured any sample peaks. Powder patterns were obtained, however, by removing small quantities of the material from the substrate; although not of the highest quality, these patterns do allow identification of the layers formed.^{34,35}

Conclusions

Growth of Cr_2S_3 at 450 °C, using $\text{Cr}(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_3$ as the precursor, produces highly crystalline layers by CVD. The layers show good uniformity in their elemental composition and structure. High quality layers were produced on a variety of substrate materials including Pyrex, Al, and Mo. Gaseous decomposition products have been found to consist of small hydrocarbons, HCN and CS_2 .

Reactions carried out using $\text{CpMn}(\text{CO})_3$ and Cp_2Fe with $\text{C}_3\text{H}_6\text{S}$ have successfully produced layers of MnS and sulfur-deficient FeS respectively on Pyrex substrates. The stoichiometry of the layers produced was found to be dependent on the flow rates of the reactants. Reactions using $\text{CpMn}(\text{CO})_3$ were found to produce the highest quality layers when an approximately 1:1 molar ratio of $\text{CpMn}(\text{CO})_3$ and $\text{C}_3\text{H}_6\text{S}$ was used, whereas at least a 1:3 ratio of $\text{C}_3\text{H}_6\text{S}$ with Cp_2Fe was needed to produce good quality layers of FeS.

The experiments using $\text{CpMn}(\text{CO})_3$ were found to produce sulfur rich layers in many cases, and it is not entirely clear how this has occurred, considering the elevated temperatures used for these experiments. However, washing of these layers with CS_2 did somewhat reduce the sulfur content so it seems probable that elemental sulfur is simply trapped within the MnS. Published work involving manganese compounds in CVD reactions has concentrated on the use of $\text{CpMn}(\text{CO})_3$ to produce MnSe^{18} layers and to dope other metal chalcogenides with manganese. No previous studies report the production of manganese sulfides from this precursor.

Reactions using Cp_2Fe were found to be more reproducible. However, not unexpectedly given the typically non-stoichiometric nature of this product, a range of composition was found for the FeS samples from 44–53% Fe. The XRD data collected were of poor quality due to the small amount of sample deposited on the substrate. It is interesting to note that CVD reactions reported by Gadgil *et al.*^{20a} give FeS_2 as the product from the reaction between $\text{Fe}(\text{CO})_5$ with $\text{C}_3\text{H}_6\text{S}$. Reactions of the pentacarbonyl with di-*tert*-butyl disulfide ($[(\text{CH}_3)_3\text{C}]_2\text{S}_2$) have also been reported^{36–38} to yield FeS_2 . By contrast films of FeS are clearly formed from Cp_2Fe in our experiments. The production of a binary sulfide with a low content of sulfur occurs notwithstanding the large molar excess of the sulfur precursor used in our experiments. This finding is in line with previous experiments where a large excess of propylene sulfide was required in the growth of thin layers of CdS .^{5,6} The compound FeS_2 is much more suitable for use in photovoltaic devices than is FeS, and it is therefore concluded that Cp_2Fe may not be so successful as $\text{Fe}(\text{CO})_5$ in the production of films for use in solar cells.

Our experiments demonstrate convenient routes to thin layers of transition metal sulfides by CVD from single-source and dual-source precursors.

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