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Modification of tin(II) sulphide thin films for solar cells

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Department of Chemistry

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Abstract

Around the world, energy demands are rising. The enormous amount of energy incident on the Earth from the Sun is still a largely untapped resource and development of solar cell technology is paramount to getting the most out of this bountiful supply. In a rapidly expanding market still dominated by silicon, the potential for next-generation thin film solar cell technologies is huge.

This work focuses on the development of a solar absorber material still in its infancy: tin(II) sulphide (SnS). It has many favourable properties making it suitable for this application and it exists in a variety of phases. The most common of these phases has anisotropic electronic properties, reducing its performance.

Recently, another phase has been characterised which does not exhibit this anisotropy and arguably has even better properties than the more common phase. As of the time of writing this new phase, known as the π-phase, has not yet been extensively tested in a solar cell.

In the first stage of this investigation, a process by which SnS could be deposited by aerosol-assisted chemical vapour deposition (AACVD) was developed. AACVD was chosen due to its scalability and relative simplicity. A single source precursor based on the well-documented and inexpensive xanthate ligand was used for this purpose. Surprisingly, deposition resulted in oxide being formed rather than sulphide. The process was thoroughly scrutinised and it was eventually deduced that it was not the process but the ligand that was responsible. Modification of the precursor solution to include a secondary reductive sulphur source resulted in formation of the pure π-phase with high crystallinity at much lower temperatures than other scalable process techniques.

With an effective method by which to deposit the material, the next phase of the investigation was to develop a cell architecture that would work for the material and make the most of its properties. As there was little information in the literature about this material’s use in solar cells, a wide selection of common solar materials were screened to determine which would be suitable to use with π-SnS. This was met with limited success - even those materials which showed some activity when paired with the π-SnS exhibited poor conversion efficiencies. This was thought to be mainly due to the morphology of the π-SnS film which had not been optimised and was found in its present state to be unsuitable for a thin film architecture.
The alloying of tin(II) sulphide with group II metal sulphides was also of interest. Previously, calcium and magnesium sulphide had been co-deposited with tin(II) sulphide by physical vapour deposition (PVD) to modify the structure and properties of the resultant material. This new alloy had a rock salt structure and boasted favourable optical and electronic properties. In order to determine whether the same results could be achieved via a chemical vapour deposition route, six novel calcium sulphide single-source precursors were developed and characterised. These too were based on the xanthate ligand.

Once again, the anomalous behaviour of the xanthate ligand was seen and optimisation of the process proved difficult. The study did however highlight the root causes of the issue and suggested some avenues of further investigation that might overcome these hurdles.

Overall this work provides a foundation from which the development and modification of π-phase tin(II) sulphide solar cells might be carried out. Further work would focus first on tackling the issues which arose in the course of this investigation, using the information gained about their origin. The results obtained in the course of these experiments suggest that with optimisation π-SnS could provide a viable alternative to the current market leaders in solar energy generation.
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Chapter 1

Introduction

This work describes the development of a process using a previously untested precursor to deposit thin films of tin monosulphide by aerosol-assisted chemical vapour deposition. The process was then used to incorporate these thin films into a solar cell so that its properties could be investigated and suitable supporting materials could be found.

The modification of tin monosulphide by the incorporation of group II metal sulphides was also of interest due to the potential for controlling the material’s structure and tuning its electrical properties. To this end, a family of precursors for calcium sulphide were developed for co-deposition with the tin precursor.

This chapter will cover the background of the deposition technique used and the current knowledge about the family of precursors employed. More specific introductions to the work covered in the subsequent chapters are found at the beginning of each chapter.

1.1 Chemical vapour deposition

Chemical vapour deposition (CVD) is a process by which thin films of material are deposited upon a substrate through decomposition or reaction of one or more chemical precursors. It has its roots far back at the end of the 19th century\(^1\) where it started to be developed as an industrial process for the production of high purity metals. More recently however it has become extremely important in the deposition of thin films and coatings. As the field of electronics has taken off it has become an invaluable technique for the fabrication of ever smaller, ever more intricate devices. Meanwhile as engineering has become more precise, requiring lower tolerances and higher performance, CVD has also become vital for many engineering applications too.
CVD is a very versatile technique, able to deposit thin, compact layers of a wide variety of materials in a controlled way. Semiconductors, metal films and insulating materials have been deposited for applications in microelectronics, energy harvesting and sensors. Ceramic films have been deposited for a huge variety of uses including refractory coatings to protect against wear, corrosion, thermal shock, diffusion and other forms of physical and chemical damage and coatings to impart new properties such as superhydrophobicity and “intelligent” response to stimulus.

There is no single design for a CVD process, rather every single application has its own optimised setup and there are many variations of the technique for different chemical systems. Despite this, a generalisation can be made that all CVD systems are essentially based around three core parts which will be discussed in the following section.

1.1.1 The CVD system

The first part of the CVD system is the delivery of the precursor. A precursor is a chemical compound that is chosen for its ability to either break down or react with another compound to form a desired product. The core principle of CVD is that the precursor chemicals used are in the vapour phase prior to deposition. As most chemicals are in a condensed state under atmospheric conditions (and tend to be easier to handle in this form), the precursor delivery system must employ a means by which the precursor can be converted into the vapour phase for use. For solid precursors this is often done through sublimation: elevated temperatures and/or low pressure are used to encourage the material into the vapour phase.

Liquids may be evaporated using a bubbler, in which a gas is blown through the liquid to cause it to evaporate at a controlled rate, or alternatively through flash evaporation where the liquid is squirted into a heated chamber to cause it to evaporate quickly and provide a pulse of vapour. The vapour is usually carried along by a carrier gas, which can either be an inert gas like argon or a reactive one like hydrogen depending upon what is required.

Having been converted to the vapour phase, the precursor is carried through to the reactor. This is a chamber in which the substrate sits and which supplies energy to activate the reaction. Energy is most commonly supplied as heat, however light and plasma are also sometimes used. Heated reactors are usually described as either “hot wall” or “cold wall.”
In a hot wall reactor the chamber is essentially a furnace. The entire chamber is resistively heated which results in uniform heating of the substrate, however this means that deposition of the product material also occurs on the reactor walls. The material must be removed in order to maintain the reactor and the reproducibility of the process.

In a cold wall reactor only the substrate is heated, either resistively or inductively. This has the advantage that deposition only occurs on the substrate, however it is more difficult to achieve uniform conditions across the substrate.

The byproducts of the reaction then pass into the exhaust system along with the carrier gas. Often the byproducts and intermediates of the reaction will be reactive or toxic and so the exhaust will involve a mechanism to scrub these gases before they are released. In some cases where the precursor is less reactive or the reaction is reversible a recycling mechanism may be present to reduce waste.

Another function that an exhaust system can have is that of monitoring. Various analytical techniques can be used to monitor the gaseous byproducts coming from the reaction. These include mass spectrometry, Raman spectroscopy and other forms of optical spectroscopy.

1.1.2 Advantages and disadvantages of CVD

CVD has a number of advantages that make it very versatile for the deposition of many different materials. First of all, the process control is very high. In other words, it is possible to have a high degree of control over what is deposited and how this occurs by careful control and modification of the deposition parameters. The technique is very flexible, meaning it can accommodate many different types of chemical reaction and so it can be used for the deposition of many different materials. It is possible to reproducibly achieve high density, compact films which is very important for many applications, especially where the layer is designed to be refractory.

CVD also has a couple of distinct advantages over physical deposition techniques. One is that it is does not require line-of-sight for deposition. This means that it is significantly less prone to shadowing caused by rough surfaces. The other advantage is that it tends to use relatively low deposition temperatures when compared to physical techniques.

The technique does have some limitations however. First of all, due to the nature of the deposition it relies on reactive precursors for efficient and controllable deposition. The upshot of this is that the many of the reactants are highly flammable (many are
pyrophoric), toxic, corrosive or a combination of these. This is arguably exacerbated by the necessity for the precursor to be volatile.

The prerequisite for volatility is another limitation in itself as it restricts the pool of viable precursors and potential materials and can increase the cost of deposition. Finally, the deposition of multicomponent species by CVD has been proven to be tricky due to the difficulty of controlling the concentrations of gases with different vapour pressures and reactivities to achieve the desired stoichiometry.

1.2 Aerosol-assisted chemical vapour deposition

Aerosol-assisted CVD (AACVD) is a variation of the classic CVD technique that seeks to address these limitations and allow for simpler deposition processes. The difference between the two techniques is summed up in its prefix - the precursor is delivered to the reaction chamber with the assistance of an aerosol. Essentially, instead of evaporating a volatile precursor, the precursor is instead dissolved in a suitable solvent. The solvent is chosen such that the solubility of the precursor is high, while the solvent has a low vapour pressure and viscosity.\(^5\) The precursor solution is turned into an aerosol, which is then transported by a carrier gas into the reaction chamber. The carrier gas is usually an inert gas (e.g. \(\text{N}_2\) or Ar), but specific reactive gases such as \(\text{H}_2\) can be used if the reaction requires it.\(^6\) A schematic of the AACVD system used in this work is shown in Figure 1-1.

The solution can be nebulised by a variety of methods. One method is to use an ultrasonic atomiser in which the solution is subjected to ultrasonic vibrations, causing a fine aerosol to be generated above the solvent surface.\(^7,8\) This method produces very small droplets with a tight size distribution,\(^2\) which can be advantageous for many applications.

Another method uses an electric field to create the aerosol through a phenomenon known as a Taylor cone.\(^9,10\) The advantage of this method is that it charges the droplets in the process. As the charged droplet evaporates the charge density on the surface of the droplet increases. Eventually the droplet reaches what is known as the Rayleigh limit.\(^11\) This is the point at which the charge density becomes so great that the repulsive forces overcome the surface tension of the solvent and the droplet disintegrates into smaller droplets.\(^2\) This increases the surface area to volume ratio (and therefore the evaporation rate) further. The process may repeat multiple times before the solvent evaporates completely.
The second advantage of charging the droplets is that they can be guided towards the substrate by biasing the substrate with the opposite charge.\textsuperscript{12} This works on the same principle as an inkjet printer and results in a high degree of control over the way in which the material is deposited, as well as improving the efficiency of deposition as less precursor is wasted. Due to the advantages that are gained from charging the droplets, the highly controlled droplet size of ultrasonic atomisation has been combined with droplet charging using a corona charging unit in a process called electrostatic-assisted aerosol jet deposition (EAAJD).\textsuperscript{13}

The final method for generating an aerosol is by far the simplest and it is the technique that is used in this work. Known as pneumatic aerosol generation, this technique relies on the introduction of a steady stream of the solution into a high velocity jet of the carrier gas.\textsuperscript{2} The turbulent gas stream breaks the solution up into small droplets and carries them through to the reaction chamber. This method is less complex as it requires no moving parts or electric field. The droplet size distribution is far less controlled and much broader than that of the other techniques due to the chaotic nature by which the droplets are generated. This method has been found particularly useful in aerosol-assisted combustion CVD, where the aerosol is fed into a flame to drive the reaction and create the product.\textsuperscript{14-16}

In the system used in this work the droplet size distribution is somewhat controlled by introducing directional and cross-sectional changes in the path of the gas stream, causing larger droplets to impact on the walls or drop out of the stream as the gas
decelerates. The rejected solution will then drain back into the pot where it is recycled. Despite these controls however, the droplet size distribution is still expected to be more broad than with other more sophisticated methods.

The droplet size is important as it will affect how the droplet will behave when it reaches the reaction chamber. If the droplets are too small, they may evaporate too early and not carry the precursor to the reaction chamber effectively. If the droplets are too large, the droplet may not evaporate at all, or may contain too much precursor to be properly vaporised before reaching the substrate.

1.2.1 Key differences between AACVD and conventional CVD

AACVD as a technique has a number of advantages over CVD and as stated earlier seeks to address some of the limitations of the latter. The first is the fact that the precursors are dissolved in a solvent rather than being vaporised directly. This significantly simplifies the precursor delivery as the precursor’s volatility is no longer an important property and heated container and vacuum systems are no longer required. Furthermore, as volatility is no longer a prerequisite for a viable precursor this expands the parameter space of potential precursors enormously. This has the effect of providing more choice of routes to a particular material as well as the potential for access to otherwise inaccessible materials.

Another factor which helps to simplify the precursor delivery is the improved ease of handling the precursors. Solutions are much more simple to handle than volatile compounds and gases and the expanded choice of precursors allows selection of chemicals with lower safety risks.

For the most part, the precursor solution can act as a single source precursor. As long as all of the reactants can be dissolved in a common solvent without reacting, they can in theory be delivered in a single solution and be deposited in a stoichiometry determined by the concentrations of components in the solution. The solution-based form also means that the precursors are well mixed which reducing inhomogeneities in the deposited film.

These factors combine to address another of the limitations of conventional CVD: AACVD gives good control of multicomponent systems. This has been demonstrated with a variety of complex materials already. Optimisation still is often needed to make sure that the correct stoichiometry is achieved however, as different components of the precursor solution may behave differently in the deposition process.
On the whole, the temperatures required for deposition in the AACVD technique are lower even than conventional CVD. This is thought to be a result of the very short diffusion distances between the reactants and intermediates during the deposition process.\(^2\)

In general the deposition rate for AACVD processes tends to be quite high.\(^{23}\) For many applications, especially industrially relevant processes, this is an extremely desirable property. This does however have the side-effect that controlled growth can be more difficult to achieve. That being said, the aerosol delivery mechanism allows for more ways in which the growth of the deposited film can be controlled. The expanded library of potential ligands and chemicals which can be used for deposition means that small adjustments in functional groups and chemical structure can be made without the danger of sacrificing the precursor’s viability through loss of volatility.\(^{24}\)

The solvent itself can also have a marked effect on the growth of the deposited film. This can manifest as a modification in the growth mode\(^{25}\) or even the deposition of an entirely different phase.\(^{26}\)

Finally, the solution-based delivery opens the door to the modification of the deposited material by addition of other chemicals not directly involved in the chemical makeup of the product. An example of this is the report by McNally et al. who used a surfactant additive in a zinc oxide precursor solution to control the crystallite formation during deposition.\(^{27}\)

AACVD has even been used to deposit composite materials. By mixing pre-formed gold nanoparticles into solutions containing a precursor, Palgrave and Parkin formed a colloidal solution. Upon deposition, the gold nanoparticles became embedded in the metal oxide matrix, forming a nanocomposite thin film.\(^{28}\)

### 1.2.2 AACVD processes

There are thought to be four processes which can occur during deposition in an AACVD reactor which can have a very strong influence on the outcome.\(^{29}\) These processes are depicted in Figure 1-2 and are described in full below.

In the first process (Process 1) the aerosol enters the reactor and directly impinges on the substrate surface. The solvent then vaporises, leaving behind the precursor as a dry precipitate. The precursor can then decompose to give the product material. As the precursor is already in the solid phase before it decomposes this is likely to lead to poor morphology and high porosity in the resulting film.
In Process 2 the solvent evaporates before reaching the surface, but the precipitated precursor does not. The solid precursor then impinges on the substrate and decomposes. Both this process and the previous one are not true CVD techniques because the precursor does not actually become a vapour at any point during the process. Instead these processes are more akin to those seen in spray pyrolysis. In order to build up a compact film, sintering and multiple layers of deposition may need to be performed.

In Process 3 the solvent evaporates close to the substrate and the precursor vaporises before reaching the substrate. The vapour then travels to the surface of the substrate and undergoes a heterogeneous reaction to form the film on the surface. This is a true CVD process and tends to lead to high quality, compact films with highly controllable growth rates.

The final process (Process 4) tends to occur when the temperature is too high. The solvent and precursor are both vaporised before reaching the surface, but the precursor vapour reacts while still in the vapour phase. Depending on the properties of the product material this may then undergo homogeneous nucleation on the substrate surface to build up a film, or alternatively it may precipitate directly out of the vapour phase to form a powder. In this second scenario, the powder is likely to be poorly adhered to the substrate if at all and much of it is likely to be wasted.

Identifying which process is happening in an AACVD reactor is not a straightforward process. Often the best way to infer the type of process occurring is through analysis of the resultant film. This information can be useful to understand which parameters may need to be adjusted and in which direction in order to achieve the desired result.
1.3 Metal xanthates as precursors for metal sulphides

The aim of this work is to deposit metal sulphides in a repeatable, controlled manner. Metal xanthates are considered to be reliable single-source precursors for metal sulphide films due to the metal-sulphur bond already being pre-formed in the complex. The xanthate ligand is bidentate and binds to the metal centre through its dithiocarboxylic acid group (see Scheme 1-3). In this figure, the R group represents an alkyl group and the $L_x$ represents the other ligands co-ordinated to the metal centre.

1.3.1 Synthesis

The synthesis of metal xanthates is a straightforward process and can be realised in more than one way. Perhaps the most basic of these involves a simple salt metathesis, where a group I metal xanthate (e.g. potassium xanthate) is reacted directly with a metal salt in a suitable solvent (this can often be water) to form the desired metal xanthate product.$^{30-49}$ Potassium xanthates are relatively inexpensive and the resulting salt can be easily separated from the product due to their dissimilar solubilities.

Alternatively, synthesis of the metal xanthate can proceed first by the procurement of the metal alkoxide followed by addition of CS$_2$, which undergoes an insertion reaction into the metal-oxygen bond and forms the xanthate.$^{40,50-54}$ A proposed mechanism for this reaction is shown in Scheme 1-4.$^{55,56}$ Again, in many instances this synthesis is cheap to perform and is also quite atomically economical.

1.3.2 Decomposition

The decomposition of xanthates is not a fully understood process. There are two different mechanisms which have been proposed to explain the decomposition of xanthate-based compounds into metal sulphides and the byproducts they release in the process. One of these mechanisms involves a Chugaev elimination reaction as the first step of decomposition.$^{57}$ The Chugaev elimination requires that the xanthate ligand has an R group with a $\beta$-hydrogen$^{54}$ (see Scheme 1-3). The reaction involves the transfer of the $\beta$-hydrogen from the R group to one of the sulphur atoms and a syn-elimination

\[
\text{RO} \quad \text{S} \quad \text{S} \quad \text{ML}_x
\]

Scheme 1-3: A representation of the structure of a metal xanthate.
Scheme 1-4: Proposed mechanism for the insertion of CS$_2$ into metal-oxygen bonds to form the metal xanthate.

resulting in the loss of the R group as an alkene (see first step in Scheme 1-5).

Alam et al. proposed a general mechanism for the thermal decomposition of metal xanthates in their 2008 report on the deposition of nickel sulphide from nickel xanthate precursors.$^{33}$ The mechanism is presented in Scheme 1-5. The first step is the Chugaev elimination of an alkene as discussed above. This is then followed by further re-arrangement and elimination of carbonyl sulphide and finally H$_2$S to result in the metal sulphide.

The report also details analysis of the thermal decomposition by thermo-gravimetric analysis (TGA). As evidence for the mechanism presented, the authors note an initial mass loss congruent with the first step of the mechanism and loss of the supporting ligands. Throughout all four of the precursor complexes studied, the intermediate residue after this initial mass loss was consistent with a metal dithiocarbonate species. A second, slower mass loss corresponded with the second and third steps of the mecha-

Scheme 1-5:  Thermal decomposition mechanism for generalised metal xanthate as described by Alam et al.$^{33}$
nism, namely the loss of carbonyl sulphide and H$_2$S. In all cases the final residue agreed well with the expected mass for NiS, the identity of which was verified by powder X-ray diffraction (PXRD) and energy-dispersive X-ray spectroscopy (EDXS).

In their report on the decomposition of lead n-butyl xanthate to form PbS films by AACVD, Akhtar et al. include the results of a DFT study of the decomposition mechanism of their precursor. Having made the assumption that the mechanism follows the pathway detailed in Scheme 1-5, they modelled each step of the process to determine the activation energies involved. They found that the first step (the Chugaev elimination) had the highest activation energy of 160 kJ mol$^{-1}$ and concluded that this would be the rate limiting step. TG analysis of their compound agreed with this finding, showing a single event for the entire decomposition of the compound and suggesting that the first step could be rate-limiting. However, TGA of other metal xanthates have shown multiple steps$^{33,37,41,42,46-48,52,59,60}$ indicating that this does not hold true for all metal xanthate systems.

Castro et al. used electron ionisation (EI) to study the fragmentation of antimony xanthates. While this is not necessarily directly analogous to thermal decomposition, the fragments detected in these experiments suggest a similar mechanism to the one determined through analysis of thermal decomposition. The authors present essentially the same mechanism for the formation of antimony sulphide, however in the final step a xanthate ligand which had been retained up until this point is then lost along with the hydrogen of the SH group attached to the metal. The mechanism of this final step or steps is not discussed in the report, but presumably it is expected to proceed either by the same process again (as suggested by Alam et al.$^{33}$), or by an intramolecular reaction where the hydrogen is passed to the unfragmented xanthate ligand, which is then lost as xanthic acid.

Castro et al. also provide evidence for the occurrence and importance of the initial Chugaev syn-elimination of the alkene through analysis of antimony methyl xanthate. They cite its "unusually high temperature for the onset of decomposition" and "poor performance in generating Sb$_2$S$_3$ films" as symptoms of the lack of $\beta$-hydrogens in the methyl xanthate ligand, meaning that the initiating Chugaev elimination cannot take place.

One of the earliest analyses of metal xanthate decomposition is found in the 1997 report by Vreugdenhil et al.$^{39}$ In this investigation the authors synthesised a variety of metal ethyl xanthates and studied their decomposition by heating the solids un-
der vacuum on a metal sample stage to temperatures of 120 °C. The evolved gaseous byproducts were studied using head-space gas-phase FT-IR.

The authors found that in their experiments decomposition seemed to begin at a significantly lower temperature than that suggested by thermo-gravimetric analysis (TGA) or differential thermal analysis (DTA). Triatomic molecular gases (CS$_2$, COS and CO$_2$) began to evolve at temperatures only a little above room temperature. Using $^{13}$C-labelling these were found to be originating from the dithiocarbonate carbon and its adjacent atoms. At higher temperatures some more complex species were also seen, but only ethanol was successfully identified.

From the atomic ratios in the detected gaseous products the authors inferred that the majority of the residues were either metal alkoxides or metal thiolates. The metal xanthates were divided into two groups depending on which of the two types of residue were apparently favoured. Small, hard cations appeared to favour the alkoxy-ligand and produce more highly sulphurised triatomic species, while the byproducts of the larger, softer cations were extremely sulphur-poor, indicating the preference for the thiolate ligand.

From these observations a set of mechanisms were proposed to explain the formation of the various triatomic gases seen in the head space of the reaction chamber. These mechanisms are shown in Scheme 1-6. All of the triatomic gases are produced in essentially the same way, the elimination of a heterocumulene to leave the metal alkyl chalcogenide. The identity of the heterocumulene released depends upon the location of the alkyl group and the manner in which the ligand is bonded to the metal. CO$_2$ was believed to be produced by the re-insertion of COS into a metal alkoxide formed by previous CS$_2$ elimination, followed by further re-arrangement and elimination of CO$_2$.

While these findings are important in the consideration of xanthate decomposition it must be noted that the temperatures used in this study are not high enough to achieve full decomposition of the xanthate.

In a similar vein, Todescato et al. annealed thin films of zinc ethyl xanthate at 200 °C, analysing the gaseous products by head space gas chromatography and mass spectrometry (HS GC-MS). They reported detection of CS$_2$ and COS, but were unable to detect CO$_2$ or ethene due to limitations of their experimental setup. They did however detect traces of acetaldehyde, ethanethiol, diethyl sulphide and diethyl disulphide, leading them to believe that a similar process of relocation of the alkyl group and elimination of the heterocumulene was also occurring here.
Scheme 1-6: Decomposition pathways for metal xanthates as described by Vreugdenhil et al.\textsuperscript{39}

Macreadie et al. also probed the decomposition by HS GC-MS. Their findings mirrored those of the previous study, namely the major components of the decomposition by-products being CS\textsubscript{2} and COS, as well as ethanol. They also detected alkanes, thi-oethers and dithioethers as minor products of the reaction. The authors note a lack of signals corresponding to ethene, leading them to conclude that the decomposition of their compound does not involve a Chugaev elimination step. They also mention the lack of a signal for H\textsubscript{2}S, which they note had been detected in other studies.

A third study involving the investigation of xanthate decomposition by HS GC-MS was conducted by Chesman et al.\textsuperscript{62} This study also detected COS, CS\textsubscript{2} and ethanol as major byproducts, alongside Et\textsubscript{2}S, Et\textsubscript{2}S\textsubscript{2} and the supporting ligand in their compound, pyridine. Lesser amounts of SO\textsubscript{2}, acetaldehyde and S-ethyl ethanethioate were also detected, along with trace amounts of ethene, ethanethiol, ethylacetate, methacrolein, thiophene, ethyl vinyl sulphide, diethyl carbonate and S-ethyl-O-ethyl dithiocarbonate. The authors postulate that the wide variety of byproducts indicates that the xanthate does not decompose by a single route, but rather through multiple competing mechanisms.

The identification of ethene in the GC-MS spectrum indicates that the mechanism involving the Chugaev elimination may well be one of these competing mechanisms, although the fact that ethene is only present in trace amounts indicates that this was likely not a major process and could also be the result of other processes. The extremely
short residence time of ethene combined with its low signal intensity may explain the absence of its signal in other studies.

The authors also conducted a combined thermogravimetric analysis/mass spectrometry study on the xanthat and noted the presence of S-ethyl-O-ethyl xanthat as a byproduct. They explain the absence of this compound in the HS GC-MS by noting that due to its high boiling point it may not be present in the gas phase in amounts large enough to be picked up by the HS GC-MS equipment. Using this information, they propose a mechanism for the production of the observed compounds, shown in Scheme 1-7.

The presence of CS₂, the alkyl sulphides and ethanol are attributed to processes beginning with the mechanisms proposed by Vreugdenhil et al. although the authors point out that these products could also be generated by the decomposition of the S-ethyl-O-ethyl xanthat. The lack of a signal corresponding to H₂S is used to suggest that the Chugaev elimination is not occurring in this decomposition and presumably the ethene is believed to be the result of a different process.

In a report by Cheon et al. the decomposition of zinc isopropyl xanthat (Zn(S₂COiPr)₂) by laser-driven CVD was studied in situ using photoluminescence spectroscopy. Before discussing the mechanisms proposed in this study it is important to note that decomposition was facilitated by a laser rather than heat. Photochemical decomposition reactions can often proceed via different mechanisms than thermal decompositions, meaning that the mechanisms described by this report cannot be directly compared to those found by thermal decomposition. It is nevertheless worth being aware of these processes to better understand the behaviour and properties of the xanthat system.

![Scheme 1-7: Mechanism for the formation of COS and S-ethyl-O-ethyl xanthat during metal xanthate decomposition as described by Chesman et al.](image-url)
By analysing the luminescent species in the gas phase along with those collected by electron impact and laser desorption time-of-flight mass spectrometry, the various processes were deduced. Notably, none of the processes described in this report involve the Chugaev reaction, instead focusing on the cleavage of Zn-S and C-S bonds. There is no mention in this report of the loss of propene, which would be expected if a Chugaev elimination was occurring. Instead propane and isopropanol are observed through study of organic byproducts collected in a liquid nitrogen cold-trap during the decomposition reaction. The presence of free xanthate ligand (iPrOCS\(_2\)), Zn(S\(_2\)CO\(_{iPr}\)) and Zn(S\(_2\)CO\(_{iPr}\))S observed by mass spectral analysis was taken as an indication of their proposed mechanism. Luminescence spectroscopy identified free Zn atoms and very hot S\(_2\), which the authors suggested would react directly to give ZnS.

A further study in the same year by the same group also studied the decomposition of nickel and lead isopropyl xanthates\(^\text{64}\). In this case only luminescence spectroscopy was used to study the reaction and once again luminescence from free metal atoms and hot S\(_2\) was seen.

Altogether, this is an entirely different path for the decomposition of the xanthate system. The processes do however still eventually lead to the formation of the metal sulphide and the observations made serve to highlight how complicated the decomposition of xanthates is.

In conclusion, there is evidence for multiple potential decomposition reactions for the xanthate system. The dominant decomposition pathway seems to be dependent upon the conditions under which the decomposition takes place. From the variety of the results collected using the same technique but different metal xanthate compounds, it is entirely possible that the identity of the metal has a strong effect on which decomposition pathway or pathways are favoured. Furthermore, there is reasonable evidence that during decomposition there are in fact multiple competing mechanisms, leading to a variety of byproducts in the process.

As demonstrated by the papers discussed above, the xanthate ligand has been combined with a variety of different metals to cleanly produce metal sulphides, including cadmium\(^\text{32,44,47,49,50,62,65-67}\), zinc\(^\text{37,39,41,60,61,63,68}\), nickel\(^\text{33,39,43,60,64}\), lead\(^\text{36,39,53,58,64}\), indium\(^\text{38,69}\), bismuth\(^\text{31,40,66,67}\), antimony\(^\text{34,40,66,67}\), tin\(^\text{35,41}\), copper\(^\text{38,39,41,42,54}\), iron\(^\text{30,48}\), arsenic\(^\text{40}\), strontium\(^\text{70}\), lanthanum\(^\text{60}\), cobalt\(^\text{60}\), palladium\(^\text{45,46}\), calcium\(^\text{51}\) and barium\(^\text{54}\).

The xanthate system has also been proven to be quite versatile in the deposition methods it is suitable for. Depending upon the R group and supporting ligands, there is a
lot of scope for tuning of the properties of the metal xanthate to suit the desired deposition technique. Metal xanthates have been designed to be volatile for techniques such as CVD\textsuperscript{37,39,63-65,68,69} or soluble in a variety of solvents for use in solvothermal synthesis,\textsuperscript{31,34,35,45,46,53} spin coating,\textsuperscript{32,38,44,48,54,61,66,67} AACVD\textsuperscript{33,34,36,41,43,45-47,49,58} and doctor-blading.\textsuperscript{38,41} This has allowed the ligand to be used for the synthesis of metal sulphides in the form of both thin films and nanoparticles.

References


Chapter 2

Theory

2.1 Solar radiation

The fusion of hydrogen nuclei to form helium releases a colossal amount of energy. Deep below the Sun’s surface at a temperature of over 20 million Kelvin, 600 million tons of hydrogen is consumed every second. The energy released sustains the fusion reaction and heats the outer layers of the Sun to approximately 5800 K, which in turn radiate this energy into space.

The electromagnetic radiation profile produced by the Sun can be described with reasonable accuracy by the black-body radiation model. This model assumes that the object is made of a material that is opaque, absorbs all incoming light and emits thermal radiation in a uniform manner. Equation 2.1, known as Planck’s law of black-body radiation, describes the relationship between the temperature of a perfect black-body and its spectral radiance.

\[
F(\lambda, T) = \frac{2\pi hc^2}{\lambda^5(e^{\frac{hc}{\lambda kT}} - 1)}
\]  

(2.1)

In this equation \( F(\lambda, T) \) is the spectral irradiance of radiation of wavelength \( \lambda \) from a unit area of a black-body at temperature \( T \) in W m\(^{-2}\) nm\(^{-1}\), \( h \) is the Planck constant, \( c \) is the speed of light in a vacuum and \( k \) is the Boltzmann constant. The equation describes a skewed bell-curve, the maximum of which can be found using Wien’s displacement law (Equation 2.2) where \( b \) is the Wien displacement constant \((2.90 \times 10^{-3} \text{ m K})\) and \( T \) is the temperature.

\[
\lambda_{\text{max}} = \frac{b}{T}
\]  

(2.2)

Using this equation, the peak maximum for a black-body at room temperature would
be at 9.7\,\mu m (deep in the infra-red), and so the object would appear black. An object with the temperature of the Sun’s surface however has a peak maximum of 500\,nm and so it glows visibly as it radiates its thermal energy.

The Earth’s atmosphere has a significant effect on the spectral irradiance profile of the Sun as measured from the Earth’s surface. Portions of the spectrum are reduced due to a combination of absorption by molecular gases and atmospheric scattering caused by microscopic particulates. This is represented by the air mass coefficient which is referred to using the acronym “AM” followed by a number. The number is a representation of the path length of atmosphere the radiation must travel through before reaching the ground. The air mass coefficient is calculated using the following equation:

\[ AM = \frac{1}{\cos(\alpha)} \] (2.3)

where \( \alpha \) is the angle from the zenith (vertical). In this way, AM1 describes the path length when the sun is at the zenith (i.e. directly overhead). Moving away from the zenith, the thickness of atmosphere the radiation must travel through increases, as does the air mass coefficient. As the angle of the sun varies with the time of day, time of year and latitude, AM1.5 is the standard used to characterise the performance of solar cells. It follows therefore that the solar spectrum outside of the Earth’s atmosphere is designated AM0 (in other words an atmospheric path length of 0).

Figure 2-1 shows the difference in spectral irradiance between AM0 and AM1.5. At shorter wavelengths the intensity is significantly reduced in the AM1.5 spectrum. There are also a number of deep troughs caused by absorption of certain wavelengths by gases in the Earth’s atmosphere. By integrating under this profile the power of the incident radiation reaching Earth’s surface is approximately 1000\,W\,m^{-2}.
Figure 2-1: AM0, AM1.5 and blackbody spectral profiles.

2.2 Electronic properties of semiconductors

In order to define a semiconductor, the electronic structure of such materials must first be understood. The basis for understanding semiconductor behaviour is rooted in band theory. In an isolated atom the electrons exist in orbitals surrounding the nucleus. When atoms interact chemically their orbitals overlap and combine, forming sets of bonding and antibonding orbitals. The number of molecular orbitals is always equal to the number of atomic orbitals used to make them, so as more atoms are added there are more energy levels for the electrons to sit in. Eventually the difference in energy between “adjacent” orbitals becomes so small that they essentially behave like a continuous band. This concept is represented in Figure 2-2.

Another key concept in understanding the electronic properties of bulk solids is the Fermi level. At room temperature, with no other external influences, most of the electrons will be in their ground state. Some electrons however will be excited into a higher energy level due to the thermal energy present. This leaves the highest occupied energy levels only partially occupied, with the population of electrons in these levels following a Boltzmann distribution. The Fermi level is therefore defined as the energy
level which is statistically expected to have an occupancy of 50%.

Materials are often grouped into three broad categories based on their electronic properties. These are metals, insulators and semiconductors. Each of these groups can be described in terms of their energy bands and Fermi levels. In a metal, the Fermi level sits within a band. This means that at room temperature the energy levels close to the Fermi level are only partially filled due to electrons being promoted to higher energies by thermal excitation. This leaves gaps in the vacated energy levels known as holes. The presence of these holes (or absence of the electrons that would usually fill them) means that other electrons are able to move through the material from one hole to the next. Given that a material has mobile electrons, if a potential is applied across the material the electrons will flow through the material, following the direction of the generated electric field. This is what gives rise to metals’ property of electrical conduction.

In semiconductors and insulators the Fermi level sits in the gap between two bands (see Figure 2-3). At 0 K the bands below the Fermi level are filled, while the ones above are empty. The filled band with the highest energy (i.e. the one closest to the Fermi level) is known as the valence band. The lowest energy unoccupied band is known as the
conduction band. Electrons must exist within available energy levels, so enough energy must be absorbed for the electron to jump across the energy gap from the valence band into the conduction band if it is to be promoted. Despite this, in ambient conditions there will always be some thermally excited electrons which have been promoted to the higher energy band. As the conduction band is otherwise unfilled, the electrons are able to move freely within the band and so will move around the material as described above. At the same time the excited electrons leave holes in the valence band, allowing movement of electrons through this band too.

The number of electrons promoted across the energy gap is determined by the size of the gap and the energy available. The larger the gap is, the more energy is required to excite an electron across it and so the lower the chance of any particular electron gaining enough energy. This population of excited electrons is known as the intrinsic carrier concentration and can be determined using Equation 2.4 below:

\[
 n_i = N_s \exp\left(-\frac{E_g}{2k_B T}\right)
\]  

(2.4)

In this equation, \( n_i \) is the intrinsic carrier concentration at a given temperature \( T \), \( N_s \) is the volume density of available states, \( E_g \) is the energy gap between the valence and conduction bands (the band gap) and \( k_B \) is the Boltzmann constant. Both \( N_s \) and \( E_g \) are material dependent, however this equation shows that as the band gap increases...
the intrinsic number of free carriers will fall. In other words, the larger the band gap
the less conductive the material will be.

Semiconductors have relatively small band gaps, meaning that while they are not as
conductive as metals there are enough free carriers that a functional current can flow
in the material. Insulators have relatively wide band gaps, meaning that they have few
free carriers and are more suited to applications intending to block the flow of current.
There is no clear definition between semiconductors and insulators as band gap energy
is a continuous scale, however semiconductors are sometimes classed as materials with
a band gap smaller than 3.0 eV while insulators have band gaps larger than this.

This is not the complete story however, as the carrier concentration is also dependent
upon a material’s density of states near its band edges. Therefore a material with a
band gap of 2.9 eV and a low density of states can be considerably less conductive than
one with a band gap of 3.1 eV and a high density of states. Furthermore, Equation
2.4 shows that the number of free carriers increases with temperature, meaning that at
elevated temperatures these materials become more conductive.

It is possible to increase a semiconductor’s conductivity by introducing defects in
the material. This is most commonly done by the inclusion of relatively small amounts
of dopant atoms. The dopants will usually replace one of the types of atoms in the
host material and will have a different number of valence electrons to the substituted
atom. This leaves the structure with either a slight dearth of electrons (excess holes)
or a slight excess.

The inclusion of a dopant with fewer electrons than the host atom leaves more holes
in the valence band as there are now more electrons missing. These holes are free
carriers, able to move through the material and conduct charge just like the intrinsic
population. This leads to an increased conductivity in the material.

As described earlier the Fermi level sits at the energy level with 50% occupancy in
the material. If there are fewer electrons, the bands are not filled up as far and so the
Fermi level drops, moving closer to the valence band (see Figure 2-3). In this way the
material will have more free holes than electrons and is termed a p-type material.

Conversely, a dopant atom with more electrons than the host results in extra elec-
trons being present in the material. The valence band is already full so these electrons
must populate the conduction band. As such they are able to travel freely through
the material and conduct charge, increasing the material’s conductivity. This time the
Fermi level is shifted towards the conduction band, again shown in Figure 2-3.
2.3 p-n junctions

Most semiconductors have an excess of either holes or electrons due to inherent defects in the material, making them either p-type or n-type respectively. In a p-type material, the holes are the majority carriers, while the electrons are minority carriers. The opposite is true in an n-type material.

When a p-type and an n-type material are brought into electrical contact with one another the excess carriers present in each material are able to pass across the interface into the other material. Close to the interface these carriers will recombine, leaving a localised area near to the interface with fewer free carriers. This is known as the depletion region (see Figure 2-4).

The ions in the materials whose charge would usually be balanced by the free carriers are now exposed, but they are fixed in the crystal lattices. This results in an electric field across the interface which the remaining free carriers can interact with. Holes entering the electric field are swept into the p-type material while electrons are swept into the n-type material, reinforcing the imbalance between the populations of charge carriers in the materials.

This can also be represented in the form of a band diagram. Referring back to Figure 2-3, the Fermi level of the p-type material is closer to the valence band, while the Fermi level of the n-type material is closer to the n-type material. When the materials are in electrical contact however the charge carriers flow from the higher energy state in one material to the lower energy state in the other, recombining with their counterparts. This counteracts the gradient in the Fermi level until it is balanced. This has the effect of shifting the band energies of the materials relative to one another, as depicted in Figure 2-5. The energy barrier created by the depletion zone is easy to see here - electrons in the p-type material move easily into the n-type material as they are moving with the electric field. They are barred from moving the other way however, as this would mean overcoming the energy barrier to do so. Holes with their opposite charge are affected in the opposite way, able to move from n-type to p-type but not the other way around.
Figure 2-4: A representation of a p-n junction.

Figure 2-5: A representation of the band structure of a p-n junction.
2.4 Solar cell structure

Solar cells work on the basis that the energy absorbed from the incident light generates extra free carriers in the cell by exciting electrons into a higher energy state and leaving behind holes. A semiconductor in isolation will still do this, but the free carriers will simply move randomly around in the material until they happen upon their counterpart and recombine, releasing their excess energy as light and heat. As described in the previous section the electric field at the interface of a p-n junction imparts a force on carriers close to the junction interface, sweeping holes into the p-type material and electrons into the n-type material and separating them so they cannot recombine. The current caused by this action is referred to as the drift current. At rest, the drift current exactly balances out the diffusion.

When light is shone on the device more free electron-hole pairs are generated. If the minority carrier reaches the depletion region it is swept across to the other material and the carriers are separated. This creates a potential difference across the cell as the drift and diffusion currents are no longer balanced. By depositing a charge collector on each side of the cell and connecting an electrical circuit across these two terminals, the potential difference will drive current around the circuit.

The exact structure of a solar cell can vary widely depending upon the materials used to make them. The most common solar cell is based on silicon. In silicon cells a silicon wafer doped with a group III element (e.g. boron) to make it p-type is doped on one side with a group V element (e.g. phosphorus) to make that side n-type. This process creates the p-n junction. The p-type side of the wafer is metallised to form one contact, while a grid of metal is printed on or otherwise attached to the n-type side to form the other contact. One contact must be a grid otherwise light will not be able to enter the cell, and the n-type side is chosen because the surface quality of n-type silicon tends to be better than that of p-type silicon. While this is the general structure of the silicon cell, most silicon cells are more complicated than this, adding anti-reflective coatings, surface texturing, doping gradients and more to enhance the performance of the cell.

Thin film solar cells often rely on two different materials to form their p-n junction. Most commonly, they use a monolithic structure where thin layers of various materials are deposited one on top of another, with a metal back contact and a transparent conducting oxide (TCO) layer to allow light into the other side. These will be covered in more detail in Chapter 5.
Organic cells also use two different materials to form a junction, however in this case the materials are made of discrete molecules. Rather than conduction and valence bands, the carriers sit in the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO). Organic junctions tend to suffer from poor charge transfer at the junction interface. To address this, the surface area of the interface is made as large as possible by creating a bulk heterojunction, where two immiscible organic materials are intimately mixed together while still maintaining electrical paths through each material to their respective contacts. Both of these cell types often employ extra layers to help filter which charges can move in which direction.

Dye-sensitised solar cells are based around a light absorbing sensitiser and a liquid electrolyte, with the sensitiser supported on a mesoporous scaffold. Charge carriers are generated in the sensitiser, which then passes one type of carrier to the electrolyte and the other to the scaffold. The electrolyte then transfers its carriers to the counter electrode.

\section{Solar cell properties}

In order to evaluate the effectiveness of a solar cell the properties of the cell must be determined. Some of these properties are intrinsic to the various materials present in the cell, while others arise from the interplay of the different materials and cannot be linked to a single aspect.

Perhaps the most fundamental properties are not so much properties of the solar cell, but rather those of the absorber material. Specifically, these are the absorber's band gap and absorption coefficient. These properties are so important because they govern everything else about how the cell operates. The band gap will determine the onset energy above which the material begins to absorb radiation. Photons with energies lower than the band gap are not absorbed because they do not have the required energy to excite the electrons across the band gap, while those with higher energies will be quickly attenuated in the material.

There is a secondary effect associated with the band gap as well. Photons with an energy equal to the band gap have just enough energy to promote an electron from the edge of the valence band to the edge of the conduction band. This electron then carries the energy that it has absorbed around the connected circuit and does work, efficiently using the energy imparted to it. Photons of higher energy will also be absorbed and will promote electrons from the valence band to a level higher up in the conduction
band. The electrons then very quickly thermalise down to the conduction band edge and the extra energy they received from absorbing a higher energy photon is lost as heat. In other words, regardless of the energy of the incident photon, the maximum amount of energy which can be extracted from it is the amount associated with the band gap energy.

Due to the profile of solar radiation (see Figure 2-1), there is a trade-off between having a small enough band gap to absorb as many photons as possible and having a large enough band gap that as much of the energy absorbed is used efficiently and not lost as heat. Assuming that a cell performs perfectly, i.e. there are no energy losses anywhere else in the device, a maximum theoretical efficiency may be calculated for a cell based on the band gap of the absorber material it employs. The curve produced by this calculation is known as the Shockley-Queisser limit after the scientists who first calculated it and is presented in Figure 2-6. The curve shows that for a high efficiency cell the band gap must be in the range of approximately 0.7 eV to 1.8 eV.

The absorption coefficient is the material’s ability to absorb photons of a particular energy and it varies with photon energy. Below the band gap the absorption coefficient is essentially 0, as the photon does not have enough energy to excite an electron from the valence band into the conduction band. At the band gap the absorption coefficient increases exponentially and then plateaus. For many semiconductors the plateau will occur at around $10^4 \text{cm}^{-1}$ to $10^5 \text{cm}^{-1}$.

The magnitude of the absorption coefficient is also dependent upon the type of electronic transition occurring in the material when a photon is absorbed. A direct transition is one where the k-vector (or crystal momentum) of the valence band maximum corresponds with the k-vector of the conduction band minimum. An electron transitioning between the two bands does not need to change momentum to move from one to the other.

In an indirect transition, the conduction band minimum has a different k-vector, meaning that the electron must interact with a phonon in the crystal in order to alter its momentum and complete the transition. This makes indirect transitions less likely, as it requires the interaction of three components rather than just two. As such, indirect transitions result in a smaller absorption coefficient.

In a similar vein, a transition can also be allowed or forbidden. This refers to whether or not the transition is in accordance with the Laporte selection rule. The rule states that an electronic transition cannot occur without a change in parity - in other words an
electron in a centrosymmetric orbital must transition to a non-centrosymmetric orbital and vice versa. If this is the case, the transition is an allowed transition and occurs readily.

A forbidden transition can still occur but it requires that the orbital is distorted in some way (e.g. through vibration) so that the rule no longer applies. As this is a transient occurrence, forbidden transitions result in a low absorption coefficient.

Quantum efficiency and spectral response are properties which arise from the action of the cell as a whole. They give similar information about the cell but are measurements of different quantities. Both are wavelength specific and are presented as a continuous spectrum. Quantum efficiency is a measurement of the efficiency with which the cell generates free carriers from incident photons of a particular wavelength. In other words, it is the ratio of the number of free carriers which come out of the cell to the number of photons of a particular energy going into it. Spectral response is also a ratio, this time between the power generated by the cell and the power incident upon it.

2.5.1 Solar cell operation

The most common way in which a solar cell is characterised is through a current-voltage (J-V) curve. In this measurement a cell is connected to a potentiostat and placed in a solar simulator, which simulates the power and radiation profile of sunlight at ground level. The voltage across the cell is swept from open circuit to short circuit and back again while the current generated by the cell is measured. This results in a characteristic
Figure 2-7: A representation of a J-V curve.

diodic curve which can be used to determine the five major properties of the solar cell.

The first of these is the short-circuit current and is obtained from the point at which the curve intersects the y axis. This is the maximum current generated by the cell and is usually measured in mA cm\(^{-2}\).

The second is the open-circuit voltage (\(V_{OC}\)), which is the voltage at which the current drops to 0 mA cm\(^{-2}\). This is the maximum possible potential difference the cell can generate and is primarily dependent upon the band gap of the absorber material, however this is only part of the story. The \(V_{OC}\) is also related to the saturation current of the device, which is strongly affected by intrinsic carrier concentration of the materials and recombination within the cell.

The next measurement of cell performance is the maximum power point (MPPT). Power is the product of voltage and current and due to the profile of the response from a solar cell there is a specific voltage and current at which the maximum power conversion efficiency (PCE) can be obtained. A representation of the power profile of a

Figure 2-8: A representation of the power profile of a solar cell and its related J-V curve.
Another more abstract measurement of the cell is known as its fill factor. The fill factor is a representation of how “ideal” a cell is and is usually expressed as a percentage or fraction. An “ideal” cell would produce its maximum current output for all voltages from 0 V up to the open circuit voltage, at which point it would instantly drop to 0 mA cm$^{-2}$. This would appear in a J-V measurement as a rectangular profile.

In a real cell this is not possible as there will always be some losses during operation. The fill factor is therefore a ratio of the cell’s true maximum power point against its ideal maximum power point (calculated by multiplying the short circuit current by the open circuit voltage).

The final and most heavily cited property is the cell efficiency (or rather power conversion efficiency). This is simply a ratio of the maximum power generated by the cell to the total power incident upon it, expressed as a percentage. As such it is reliant upon all of the other properties described and describes the overall effectiveness of the cell.

### 2.6 Optical measurements of thin films

Determination of the optical band gap of a material is usually accomplished using absorption spectroscopy in the ultraviolet, visible and near-infra-red regions of the electromagnetic spectrum. This technique is often referred to as UV/Vis spectroscopy.

The absorption profile of a semiconductor is usually almost 0 at energies lower than the band gap. Upon reaching the band gap the rate of absorption increases rapidly and for a highly absorbing material will often plateau at nearly 100% absorption, even when there is only a thin film present.

It is not possible to directly measure absorption of a thin film material, as the absorbed photons are no longer available to be detected. Instead, the transmitted and reflected radiation are measured and this is then used to work out what has been absorbed.

Historically, the most common use for UV/Vis spectroscopy has been the study of solutions. For these measurements the reflection can be taken into account in the background by using a blank solution in an identical vessel and so only the transmitted signal is required to determine the absorption. This leads to the relatively simple
relationship:

\[ A = \log_{10} \left( \frac{I_0}{I} \right) = \varepsilon CL \]  

(2.5)

In this equation, \( A \) is the absorbance, \( I_0 \) is the incident intensity and \( I \) is the transmitted intensity. The second part of the equation is the Beer-Lambert law, describing the absorbance in terms of the extinction coefficient \( \varepsilon \), the concentration \( C \) and the path length through the absorbing medium \( L \). The extinction coefficient is a property of the absorbing species in a particular solvent.

When it comes to a solid thin film supported on a substrate however, the Beer-Lambert law no longer applies. The first reason for this is that the reflections of the various interfaces that the light must pass through can no longer be accounted for in the background, as there is no “blank” for a solid film. Secondly, the absorption of light in a solid medium is related to the extinction coefficient in a different way, described in the equation:

\[ I_x = I_0 e^{\frac{-4\pi f \varepsilon x}{c}} \]  

(2.6)

Where \( f \) is the frequency of the light, \( x \) is the path length through the solid and \( c \) is the speed of light in a vacuum. This equation is derived from the progressive wave equation, which described the movement of a wave through a solid, however the derivation is beyond the scope of this brief introduction. The absorption coefficient is then defined as:

\[ \alpha = \frac{4\pi f \varepsilon}{c} \]  

(2.7)

which for a thin film gives the relationship

\[ I = I_0 e^{-\alpha x} \]  

(2.8)

where \( x \) is the thickness of the thin film. Having established this, the reflection of the light at the interfaces of the thin film must also be accounted for and the following model can be constructed.

The incident light first encounters the interface between the air and the front surface of the film. Some fraction of the light, \( R \), is reflected, while the rest, \( (1 - R)I_0 \), passes into the film. In its journey through the film, some of the light is absorbed by the film in accordance with Equation 2.8 and so the intensity at the back interface (between the film and the substrate) is \( (1 - R)I_0 e^{-\alpha x} \).
At this second interface, a portion $R(1 - R)I_0e^{-\alpha x}$ is again reflected back into the film, while $(1 - R)^2I_0e^{-2\alpha x}$ is transmitted out of the film. The internally reflected beam travels back to the front interface of the film, arriving with an intensity of $R(1 - R)I_0e^{-2\alpha x}$. Another partial reflection happens, some intensity being lost out of the front face of the film, the rest reflected back into the film again. This process is depicted in Figure 2-9.

The transmittance is the light that is lost out of the back of the film, so in this model transmittance is related to reflectivity by the infinite series:

$$T = (1 - R)^2I_0e^{-\alpha x} + R^2(1 - R)^2I_0e^{-3\alpha x} + R^4(1 - R)^2I_0e^{-5\alpha x} + \ldots$$  \hspace{1cm} (2.9)

This series can be approximated to

$$T = \frac{(1 - R)^2e^{-\alpha x}}{1 - R^2e^{-2\alpha x}}$$  \hspace{1cm} (2.10)

For a highly absorbing material, such as the absorber in a solar cell, the product of $\alpha x$ is very large and the second term in the denominator can be approximated to 0. This leaves the relationship

$$T = (1 - R)^2e^{-\alpha x}$$  \hspace{1cm} (2.11)

Having derived this expression for the relationship between transmittance, reflectivity and absorption coefficient, the absorbance can now be calculated.
Equation 2.11 with Equation 2.8 and the first part of Equation 2.5 gives

\[ T = \frac{I}{I_0} (1 - R)^2 \]  

(2.12)

\[ A = -\log_{10} \left( \frac{T}{(1 - R)^2} \right) \]  

(2.13)

The transmission spectrum of a thin film is captured in very much the same way as with a solution. The film is placed in the path of the beam and normal to the direction of the beam. The intensity of the light emerging from the other side of the film is collected as the transmission spectrum.

Reflections are made up of two separate parts, specular and non-specular reflection. Both types of reflection are always present, however the portion of each is related to the roughness of the film. Specular reflection is the reflected light whose angle of reflection matches the angle of incidence. This type of reflection becomes more prevalent for smoother films. The non-specular (or diffuse) reflection is the portion of light which interacts with the surface roughness and so comes off with no definite angle of reflection. In other words, the diffuse reflections come off at all angles equally.

In order to measure the reflection spectrum of the film, both types of reflection must be collected. The film is placed at one entrance to an integrating sphere such that the incident beam enters the sphere from the “antipode” and hits the film. The diffuse reflection comes off at all angles but is captured by the integrating sphere.

This poses a problem for the specular reflection however. If the film is placed flat against the sphere with the normal of the surface parallel to the incident beam, the specular reflection will bounce back in the same direction as it had come, exiting the integrating sphere through the same hole it entered. To address this, a low-angle (e.g. 8°) wedge is introduced between the film and the sphere. This has the effect of offsetting the incident beam by the same small angle to the film normal, so the angle of reflection will also be the same low angle. The specular reflection now strikes the inner wall of the integrating sphere and is collected.

This measurement is not completely accurate however. Firstly, in order to capture all of the reflected light the entrance and exit holes in the integrating sphere would have to be infinitely small. This is not possible if the incident beam is to enter the sphere, so a small amount of the reflections are lost out of the holes. Secondly, angling the film changes the path length of the incident beam through the film, in effect changing the thickness. This will introduce error into the measurement, but as long as the angle is
kept as minimal as possible the path length discrepancy will be low. Finally, while the
equations relate absorbance to reflectivity, what is being measured is in fact reflectance.
This is used as an approximation for reflectivity, which is a bulk material property.
Despite these compromises, the accuracy of the measurement is still great enough to
obtain sufficiently accurate results.

2.6.1 The Tauc transformation

It is possible to simply plot the absorption of a thin film against photon energy, find
the step in the spectrum corresponding to the absorption onset as the photons surpass
the energy required to promote electrons across the band gap. The onset can then be
interpolated from the linear regions of the profile and a value for the band gap can be
acquired. In some cases this will give a reasonable estimate for the band gap. Depending
upon the properties of the material however, this can be very difficult. One complication
is the possibility for multiple band edges to appear at similar energies. This can happen
when a material has multiple band maxima or minima at similar energies but with
different values of crystal momentum.

Another much more common issue is the influence of surface effects and defects. Near the surface of a material the crystal structure of the material is different from the bulk due to the loss of crystal coherence at the interface. The atoms will relax in their positions to minimise the energy of the surface, leading to a distortion of the lattice and the molecular orbitals which hold the crystal together. Defects have a similar effect on the crystal in their vicinity. This in turn has an effect on the density of states near the disturbance, changing the location of band minima and maxima and subtly changing the band gap.

The effect of this is that the band gap is subtly different at different points in the material. Rather than a precise, well defined onset there is a distribution of band gaps, leading to a more gradual onset of the absorption edge. This phenomenon is known as an Urbach tail and can lead to there being no linear portion of the absorption increase at all, making determination of the onset little more than guesswork. This effect is particularly prevalent in thin films due to their morphology. Their high surface area to volume ratio means that surface effects have a disproportionately strong influence on the measurement.

In order to mitigate the effects of the Urbach tail, a mathematical transformation
may be performed on the data which minimises its contribution. This is known as the
Tauc transformation and the plots which arise from it are known as Tauc plots. The Tauc transformation is performed by plotting photon energy against \((\alpha h\nu)^{1/r}\), where \(\alpha\) is the absorption coefficient, \(h\nu\) is the photon energy and \(r\) denotes the type of the transition which gives rise to the absorption onset. \(r\) can take the following values:

- \(r = \frac{1}{2}\) for a direct allowed transition
- \(r = 2\) for an indirect allowed transition
- \(r = \frac{3}{2}\) for a direct forbidden transition
- \(r = 3\) for an indirect forbidden transition

Despite the relation of absorption coefficient to the measured transmission and reflection of the film requiring the film thickness, it is still possible to produce a Tauc plot without knowing the thickness of the film. If the film thickness is not known, a value for \(\alpha x\) is instead calculated and the Tauc formula becomes \((\alpha x h\nu)^{1/r}\) instead. Due to the nature of the transformation, the inclusion of the thickness does not affect the shape of the trace, only its scale. As such, the reading for the band gap remains the same regardless of the value of the film thickness.

If the correct value of \(r\) is selected the Tauc trace will usually be almost horizontal below the band gap energy. The gradient will then increase around the band gap energy after which point the trace will enter a linear region. After the linear region the trace can deviate in either direction. By extrapolating the linear region back, the intercept with the x-axis gives a value for the band gap. This is still an approximation but it is usually well within experimental error.
Chapter 3

Methods

3.1 General experimental methods

3.1.1 Materials

Unless otherwise stated, all materials were obtained from Sigma-Aldrich and were used as received.

3.1.2 Cleaning of glass substrates

Solaronix TEC-15 FTO glass was cleaned by sonication for 10 minutes in the following solvents: 2% Hellmanex (detergent) solution, deionised water, ethanol, acetone and isopropanol in that order. They were then air dried using a flow of nitrogen gas. The cleaned glass substrates were then placed in a Bioforce Nanosciences ProCleaner 220 UV/ozone cleaner for 20 minutes to passivate the surface and improve hydrophilicity. Once the cleaning process was complete the substrates were used immediately.

3.1.3 Preparation of silicon wafer substrates

The silicon wafer was placed in the UV/ozone cleaner for 20 minutes in order to passivate the surface and improve hydrophilicity.

3.2 Baseline correction by asymmetric least squares smoothing

A great deal of experimental data collected (particularly spectroscopic data) consists of a data series involving some form of baseline upon which a series of peaks is superimposed.
This will usually be accompanied by background noise due to the inherent limits in the sensitivity of the analytical equipment.

The baseline can have the effect of distorting the data and making extraction of pertinent data such as peak positions and areas less precise. Unfortunately in many cases the true baseline for a set of data cannot be experimentally determined and so for baseline correction to be carried out a reasonably accurate baseline must be simulated based on the experimental data.

There are many different algorithms which have been proposed and tested for this purpose. Where pertinent in this work, an algorithm using the asymmetric least squares smoothing (ALSS) approach was used to generate the simulated baseline. This was then subtracted from the raw data before the data was processed further.

ALSS has a number of advantages that make it particularly useful and effective for the type of data presented in this work. First of all it is very fast to compute: even with datasets containing tens of thousands of data points, a baseline can be generated in less than a second. This makes it possible for a tool using this algorithm to be interactive, calculating and recalculating the baseline as the user adjusts parameters in real-time. Secondly, it requires only two parameters for calculation of the baseline. The first defines the “flexibility” of the baseline, or how responsive it is to changes in the raw signal. The second defines the “position” of the baseline relative to the data, where it sits relative to the raw signal. Both of these parameters will be explained in more detail later. Finally, given the raw dataset and the two parameters described above the baseline is entirely repeatable.

While the process of finding suitable parameters for an accurate baseline can be automated to some degree this has not shown to be foolproof. Therefore human judgement is still necessary to ensure reliability of the result.

ALSS is based on an algorithm first proposed by Whittaker in 1922 which is designed to smooth a signal by least squares smoothing. The goal of the algorithm is that for a series of data $y$ of length $m$, a smoothed series $z$ can be generated such that is a) faithful to the original data $y$ and b) smooth.

These criteria can be expressed in the formula shown in Equation 3.1:

$$S = \sum_i (y_i - z_i)^2 + \lambda \sum_i \Delta^2 z_i^2$$  \hspace{1cm} (3.1)

In this equation the first term is a sum of least squares difference between the original data and the generated series and as such addresses the first criterion. The second term
describes the smoothness of \( z \) by quantifying the differences in \( z \) as a function of \( i \).

Here, the second-order differences are calculated, such that

\[
\Delta^2 z_i = (z_i - z_{i-1}) - (z_{i-1} - z_{i-2})
\]  

(3.2)

The second order differences are used as this provides a good compromise between the flexibility of the generated data and speed of computation.\(^2\) The contribution of this smoothing penalty to the overall measure of fit \( S \) is modified by the parameter \( \lambda \). The \( \lambda \) parameters is the first of the two parameters used to define the baseline, referred to as the baseline’s “smoothness”.

With this approach a signal can be symmetrically smoothed, however this is not sufficient to estimate the baseline of the signal as positive and negative deviations will be weighted equally, causing over-estimation of the baseline in the vicinity of peaks in the signal. To account for this a vector of weights \( w \) is introduced into the equation such that:

\[
S = \sum_i w_i (y_i - z_i)^2 + \lambda \sum_i (\Delta^2 z_i)^2
\]  

(3.3)

Equation 3.3 can be expressed in terms of matrices as follows:

\[
(W + \lambda D^T D)z = Wy
\]  

(3.4)

where \( W = \text{diag}(w) \) and \( D \) is a difference matrix such that \( Dz = \Delta^2 z \).

In the vast majority of datasets the peaks resulting from the sample of interest will either be all positive (above the baseline) or all negative (below the baseline). The goal of the computation for a signal with positive peaks is to calculate \( z(p) \) such that \( w \) conforms to \( w_i = p \) if \( y_i > z_i \) else \( w_i = 1 - p \). This would be reversed for a signal with negative peaks. The value \( p \) is the second parameter defining the baseline, referred to as the “asymmetry”.

Computation proceeds in a reasonably straightforward manner by using the method outlined in Figure 3-1. Figure 3-2 illustrates an example dataset collected by Raman spectroscopy. The raw spectrum in Figure 3-2a shows a series of peaks superimposed on a significant background signal. A background spectrum, calculated by the above algorithm, has been superimposed on it. Figure 3-2b shows the processed spectrum after the calculated background has been removed.

Using Python 3.6 this method can be implemented in relatively few lines of code:
Start with uniform weights \( (w_i = 1) \)

From weights calculate approximate solution \( \tilde{z} \)

From \( \tilde{z} \) calculate approximate weights \( \tilde{w} \)

Has \( \tilde{w} \) converged?

No

Yes

End

Figure 3-1: A representation of the computational method used by the ALSS algorithm.

Figure 3-2: Example raw Raman data with calculated baseline a) and baseline subtracted data b).
import numpy as np

def IsConverged(old, new, factor):
    for a, b in zip(old, new):
        if sqrt(((b-a)/a)**2) > factor:
            return False
    return True

def ALSBaseline(y, lam, p, convergence=0.05, n_iter=10):
    # Set up initial variables
    m = len(y)
    D = sparse.diags([1, -2, 1], [0, -1, -2], shape=(m, m-2))
    w = np.ones(m)
    z = np.ones(m)

    # Generate new solution based on previous values until converged
    # or out of iterations
    for i in range(1, n_iter):
        W = sparse.spdiags(w, 0, m, m)
        Z = W + lam * D.dot(D.transpose())
        z = spsolve(Z, w*y)
        old_w = w
        w = (p if y > z else 1-p)
        if IsConverged(old_w, w, convergence):
            break

    return z

The returned value from this function contains the converged baseline. A limit was set on the maximum number of iterations in the event of non-convergence but the function rarely required more than five or six iterations to achieve the required level of convergence. In none of the instances this function was used was the limit reached.

Eilers and Boelens state that empirically they have found that good ranges for $\lambda$ and $p$ are $10^2 \leq \lambda \leq 10^9$ and $0.001 \leq p \leq 0.1$. This was corroborated by observations made in this work.

Determination of a good value for $\lambda$ involved comparing the calculated baseline to the raw data. Ideally the baseline would follow the signal everywhere except where there were peaks in the signal. Determination of the value for $p$ was a little more involved.
A histogram of the residuals $y - z$ was generated and analysed. For a good value of $p$ the histogram would exhibit a peak with normal distribution centred around zero. This distribution arises from the experimental noise, upon the middle of which the baseline ought to sit. There should also be an asymmetric component in the direction of the peaks in the raw signal, arising from the peaks themselves.

Once a satisfactory baseline had been produced the baseline was subtracted from the data to produce the baseline subtracted data that could then be processed further.

### 3.3 Instrumentation

Combined TGA-MS was performed using a Setaram Setsys Evolution TGA 16/18. The sample was contained in a 170$\mu$L alumina crucible. The temperature was ramped between 30$^\circ$C and 500$^\circ$C at a rate of 5$^\circ$C min$^{-1}$. The blanket gas used during these experiments was Ar at a flow rate of 20 mL min$^{-1}$. The evolved gases were removed from the analytical chamber through a stainless steel capillary to a Pfeiffer Vacuum Omnisat GSD 320 mass spectrometer. A m/z range of 0 to 200 was scanned, each scan taking approximately 40 seconds.

Raman spectroscopy was performed on a Renishaw inVia system with a 532 nm laser source. Measurements of the sample were usually performed at 50x magnification with a scan range of 50 cm$^{-1}$ to 1820 cm$^{-1}$ and a laser power of 1%.

Scanning electron microscopy was performed using a Jeol JSM-6480LV with attached Oxford INCA X-ray analyser for EDXS measurement. An accelerating voltage of 10 kV was used and the system was calibrated using Si wafer. High-resolution imagery was captured using a Jeol JSM-6301F FESEM at an accelerating voltage of 5 kV.

Powder X-ray diffraction was performed on a Bruker D8 Advance Bragg-Brentano system with Cu K$\alpha$ source. Samples were rotated to avoid issues relating to preferential orientation. Angles between $2\theta = 20^\circ$ and $2\theta = 80^\circ$ were recorded. Signal intensity was measured in counts.

X-ray photo-electron spectroscopy was performed by collaborators at SPECIFIC, University of Swansea.

UV/Vis spectroscopy was performed on a PerkinElmer Lambda 750S UV/Vis/NIR spectrometer with 60 mm integrating sphere. Reflection measurements were collected by offsetting the sample with an 8$^\circ$ wedge so that both the specular and non-specular components of the film’s reflection were collected.

Single-crystal X-ray crystallography was performed on an Agilent Xcalibur with Mo
Kα source. The crystal was held at 150 K in a nitrogen gas stream.

NMR spectroscopy was performed on a 500 MHz Agilent ProPulse spectrometer using deuterated benzene (C$_6$D$_6$) as the solvent. $^1$H and $^{13}$C NMR was referenced internally to the residual $^1$H and $^{13}$C present in the deuterated solvent. Instrument frequencies were 500 MHz for $^1$H and 125.7 MHz for $^{13}$C. Chemical shifts are recorded in parts per million (δ) relative to the solvent peaks (C$_6$D$_6$: $^1$H, δ7.16; $^{13}$C, δ128.1). Coupling constants (J) are reported in Hz.

Elemental analysis was obtained from the elemental analysis service at London Metropolitan University.

Differential scanning calorimetry was performed on a TA Instruments QSeries DSC Q20 analyser. Samples were contained within a sealed aluminium pan. The blanket gas used was nitrogen with a flow rate of 18 mL min$^{-1}$. Samples were heated from 30 ºC to 400 ºC at a rate of 5 ºC min$^{-1}$.

Solar cell testing was performed used a TS Space Systems AAA-grade solar simulator with a halide lamp and AM1.5 filter. The solar simulator was calibrated to provide an irradiance of 100 W m$^{-2}$. Measurements were taken using a Keithley 2601A source meter.

3.4 Chapter 4 experimental methods

3.4.1 Synthesis of Sn(S$_2$COEt)$_2$ by water method

This method is based on the preparation described by Kociok-Kohn et al.$^4$ SnCl$_2$ (5.0 g, 26.4 mmol) was measured into a conical flask. 300 mL water was added to the flask and the mixture was stirred to form a white suspension. The flask was immersed in an ice bath and stirring continued. In the same way, KS$_2$COEt (8.5 g, 53.0 mmol) was added to a second conical flask and a further 100 mL water was added to it. The second flask was agitated and the KS$_2$COEt quickly dissolved to form a yellow solution. Once the first flask containing the SnCl$_2$ suspension was cold, the KS$_2$COEt solution was slowly added to it, allowing time for heat to dissipate. A pale yellow solid immediately began to precipitate. Once all of the KS$_2$COEt solution had been added the mixture was left to stir for one hour. The mixture was then filtered with a Buchner funnel and the resulting yellow solid was washed with a small amount of diethyl ether. Air was pulled through the solid for a few minutes to aid drying. The solid was loaded into a round-bottomed flask, which was attached to a Schlenk line and vacuum was pulled on
it overnight to remove the remaining solvent. The pale yellow solid was collected and stored at 0 °C. Yield: 7.2 g (76%). NMR \( \delta_{\text{H}} \) 0.83 (3 H, t, \( J = 7.1 \), CH\(_3\)CH\(_2\)OCS\(_2\)), 4.06 (2 H, q, \( J = 6.8 \), CH\(_3\)CH\(_2\)OCS\(_2\)); \( \delta_{\text{C}} \) 14.02 (CH\(_3\)CH\(_2\)OCS\(_2\)), 71.09 (CH\(_3\)CH\(_2\)OCS\(_2\)), 227.16 (CH\(_3\)CH\(_2\)OCS\(_2\)); \( \delta_{\text{Sn}} \) −606.69.

### 3.4.2 Synthesis of Sn(S\(_2\)COEt\(_2\)) by anhydrous method

This method is based on the preparation described by Raston et al.\(^5\) SnCl\(_2\) (5.0 g, 26.4 mmol) was measured into a Schlenk flask. 60 mL THF was added and the mixture was stirred to form a hazy colourless solution. KS\(_2\)COEt was loaded into a separate Schlenk flask and a further 60 mL THF was added, forming a pale yellow suspension. The flask containing the suspension was immersed in an ice bath and the suspension was stirred. The SnCl\(_2\) solution was added drop-wise to the KS\(_2\)COEt suspension using a cannula. The KS\(_2\)COEt began to dissolve into the solution as it reacted. The solution turned a strong yellow colour and a fine white precipitate formed. Once all of the SnCl\(_2\) solution had been added the solution was stirred for one hour. The resulting yellow mixture was filtered through a filter stick with filter aid and collected in another Schlenk flask. The solvent was removed by evaporation, leaving a yellow solid. The solid was loaded into a round-bottomed flask and stored at 0 °C. Yield: 7.3 g (77%). NMR \( \delta_{\text{H}} \) 0.83 (3 H, t, \( J = 7.1 \), CH\(_3\)CH\(_2\)OCS\(_2\)), 4.06 (2 H, q, \( J = 6.8 \), CH\(_3\)CH\(_2\)OCS\(_2\)); \( \delta_{\text{C}} \) 14.02 (CH\(_3\)CH\(_2\)OCS\(_2\)), 71.09 (CH\(_3\)CH\(_2\)OCS\(_2\)), 227.16 (CH\(_3\)CH\(_2\)OCS\(_2\)); \( \delta_{\text{Sn}} \) −606.69.

### 3.4.3 Aerosol-assisted chemical vapour deposition of SnS

This is a general overview of the procedure carried out for the deposition of SnS by AACVD. Specific parameters are given in the discussion in Chapter 4 where appropriate.

50 mL to 100 mL carrier solvent was measured into a conical flask, to which the solid precursor was added. The solid dissolved easily, so the mixture was agitated until a clear yellow solution was formed. The solution was poured into the stainless steel bubbler, which was closed and sealed.

In the meantime the substrates were prepared. For the experiments conducted in this chapter, the main substrates used were float glass and silicon wafer. These substrates were cleaned by the procedures described in Sections 3.1.2 and 3.1.3 respectively.

The bubbler was attached to the nebuliser and the chosen substrates were placed on a glass sheet which was placed inside the reaction tube to direct the flow of the aerosol over the substrates. The glass sheet rested on a graphite block, which had the effect of
equalising the temperature across the heated area of the reaction tube. The substrates were placed such that they were directly above the graphite block on the glass sheet. Two heating elements were placed against the reaction tube, one directly above and one directly below the graphite block. A temperature probe was inserted into the reaction tube and placed on the substrate so as to measure the temperature at the surface of the substrate.

Once the substrates had been loaded into the reaction tube, the system was sealed. A flow of nitrogen gas at 15 psi (corresponding to a flow rate of 1.25 L min$^{-1}$) was introduced through the nebuliser and the temperature controller was activated. The system was left in this state for 30 minutes to allow for residual air to be removed from the reaction tube and for the temperature to stabilise at the desired value.

Once this time had elapsed, the valves to the bubbler were opened and the precursor solution was drawn up to be turned into an aerosol in the nebuliser, as explained in Section 1.2. The deposition was run over the course of 30 minutes, after which time the heating elements were switched off. The gas flow was temporarily switched to bypass the nebuliser so that the remaining solution would run back down the tubes into the bubbler. The valves were closed and the gas flow through the nebuliser was re-established. The system was left to cool to room temperature with the flow of nitrogen gas through the reaction tube.

3.5 Chapter 5 experimental methods

3.5.1 Patterning of FTO glass substrates

The TEC-15 FTO glass substrates were masked with Kapton tape such that a central section of the square substrate was left unmasked. A small amount of powdered zinc was distributed along this unmasked area and a pipette was used to drop a few drops of 2 M hydrochloric acid onto the substrate. A cotton bud was used to spread the solution across the unmasked area and mix in the zinc powder. The FTO layer began to turn brown where it was exposed to this mixture, and could be mechanically removed using the cotton bud. Once the film had been removed in the exposed area the substrate was washed thoroughly with deionised water. The Kapton tape was removed and the substrates were then cleaned in preparation for deposition. A representation of the patterned layer can be found in Section 5.2.
3.5.2 Planar TiO$_2$ layer

Prepared substrates were placed into a metal mask designed to pattern the layer for the fabrication of a solar cell. The mask was then placed in a furnace at 500 °C for 10 minutes. In the meantime, titanium diisopropoxide bis(acetylacetone) (1 mL, 75 wt% in IPA) was diluted with ethanol 9 mL and mixed thoroughly. The solution was then transferred into a glass hand-operated spray nozzle. The mask was transferred to a hotplate set at 500 °C and covered with foil to mitigate heat loss. A timer was started at this point. After 30 seconds, the foil was lifted, the solution was sprayed once onto each pair of substrates and the lid was then replaced. This action was repeated every 30 seconds until the timer read 5 minutes and 30 seconds. The mask was then transferred back to the furnace for a further 10 minutes. Finally, the mask was removed from the furnace and allowed to cool to room temperature.

3.5.3 Mesoporous TiO$_2$ layer

Mesoporous titania paste (117 mg, DyeSol DSL 30NR-D) was measured out into a vial and ethanol (410 mg, approx. 0.52 mL) was added to achieve a 2:7 mixture. The mixture was stirred for 10 minutes to allow proper mixing. Prepared substrates were placed onto a spin coater and 130 µL of the mesoporous titania solution was dropped onto it. The solution was allowed to spread until it fully covered the surface. The spin program was then started and the substrate was spun at 6000 rpm for 30 s.

Once the spin program was complete the substrate was placed first on a hotplate at 150 °C for 15 minutes with a foil cover and finally in a furnace at 500 °C for 30 minutes. The substrates were then removed and allowed to cool to room temperature.

3.5.4 ZnO layer

Zinc bis(acetylacetone) (0.52 g, 2.0 mmol) was stirred with a mixture of methanol (20 mL) and glacial acetic acid (1 mL) until all the solid had dissolved. The clear solution was loaded into the bubbler and the prepared substrates were placed in the reaction tube of the AACVD rig. The carrier gas used was N$_2$ at 15 psi (1.25 L min$^{-1}$ flow rate). The system was allowed to equilibrate for 30 minutes while the temperature stabilised at 400 °C. Once this was achieved the solution was sprayed into the reaction tube for 10 minutes. The spray was then shut off and the substrates were allowed to cool to room temperature while the flow of carrier gas continued.
3.5.5 SnS$_2$ layer

SnCl$_2$ (1.9 g, 10 mmol) and NH$_4$NO$_3$ (1.6 g, 20 mmol) were dissolved in ethanol with stirring and the addition of HNO$_3$ (1 mL). Once complete dissolution had occurred thiourea (1.52 g, 20 mmol) was added. As the thiourea dissolved a white solid precipitated from the solution. This was filtered off and the resulting pale yellow solution was transferred into the bubbler. The prepared substrates were loaded into the reaction tube of the AACVD rig. The system was allowed to equilibrate for 30 minutes with N$_2$ carrier gas at 15 psi (1.25 L min$^{-1}$ flow rate) while the temperature stabilised at 300 $^\circ$C. Once this was complete the solution was sprayed for 10 minutes to form a yellow film on the surface. After this time the spray was shut off and the substrates were allowed to cool to room temperature while the flow of the carrier gas continued.

3.5.6 NiO layer

Nickel(II) acetate tetrahydrate (50 mg, 0.2 mmol) was dissolved in 2-methoxyethanol (1 mL) with stirring, resulting in a turquoise solution. Ethanolamine (12 µL) was added, changing the solution to a blue colour. The solution was filtered using a syringe filter with pore size 0.45 µm. The prepared substrates were placed in the spin coater and 100 µL of the solution was dropped onto the surface. The spin program was started immediately, with the substrate being spun at 3000 rpm for 30 s. Once complete, the substrate was removed and a cotton bud soaked in 2-methoxyethanol was used to pattern the film by removing the areas at the edge of the substrate where the FTO electrical contact would be made. The substrate was then placed on a hotplate at 500 $^\circ$C for 25 minutes with a foil lid, followed by annealing in a furnace at 500 $^\circ$C for 10 minutes. The substrates were then allowed to cool to room temperature.

3.5.7 PCBM layer

95% C$_{70}$ PCBM (20 mg, Ossila M113) was suspended in chlorobenzene (1 mL) by stirring and heating to 50 $^\circ$C. The solution was then filtered using a syringe filter with pore size 0.45 µm. The prepared substrates were placed in the spin coater and 100 µL of the solution was dropped onto the surface. The spin process was started immediately, with the substrate being spun at 3000 rpm for 30 s.
3.5.8 SnO layer

SnCl$_4$$\cdot$5H$_2$O (2.54 g, 7.24 mmol) was dissolved in deionised water (250 mL) at 50°C with stirring for 10 minutes. The prepared substrates were suspended in the solution for a further 10 minutes, during which time the stirring and heating continued. After the deposition the substrates were removed from the solution and washed with deionised water. The substrates were then placed on a hotplate at 250°C for 30 minutes. The substrates were then allowed to cool to room temperature.

3.5.9 Mesoporous carbon layer

The prepared substrate was placed on a flat surface and taped down such that the tape covered two edges of the substrate and acted as a mask, masking the area where contact to the FTO would be made. A small amount of carbon paste (Gwent Electronic Materials) was spread on a plastic blade. The blade was placed such that it bridged the two pieces of tape. The blade was drawn down over the substrate smoothly, leaving an even covering of carbon paste. The paste was patterned to split the cell into individual pixels and the substrate was left in the air for 10 minutes to allow the paste to dry. The substrates were then transferred to the furnace at 400°C for 30 minutes. After this the substrates were allowed to cool to room temperature.

3.5.10 PEDOT:PSS layer

PEDOT:PSS solution (Ossila M121 1.3 wt % to 1.7 wt % in water) was filtered using a syringe filter with pore size 0.45 μm. The prepared substrates were placed in the spin coater and 100 μL of the solution was dropped onto the surface. The solution was manually spread across the surface and then the spin program was started. The substrate was spun at 3500 rpm for 45 s. After the spin program had completed the substrates were placed on a hotplate with a foil lid for 10 minutes at 150°C. The substrates were then allowed to cool to room temperature.

3.5.11 ZrO$_2$ layer

The prepared substrates were placed in a metal mask designed to pattern the layer for fabrication of a solar cell. The mask was placed in a furnace at 500°C for 10 minutes. Meanwhile zirconium(IV) propoxide solution (900 μL, 70 wt% in 1-propanol) was diluted with ethanol (4.55 mL) and mixed thoroughly. The solution was then loaded into a glass hand-operated sprayer. The mask was transferred to a hotplate at 500°C and covered
with a foil lid and a timer was started. After 30 seconds the lid was lifted, the solution was sprayed once on each pair of substrates and then the lid was replaced. This was repeated every 30 seconds until the timer read 5 minutes and 30 seconds. The mask was then transferred back into the furnace for a further 10 minutes. Finally, the mask was removed and allowed to cool to room temperature.

3.5.12 Spiro-MeOTAD layer

Spiro-MeOTAD (96.57 mg, 79 mmol) was added to chlorobenzene (1 mL) and stirred for 15 minutes to achieve a yellow solution. Li-TFSI solution (30.2 µL, 0.61 M in MeCN) and tert-butyl pyridine (9.6 µL) were then added to the solution, which was stirred for a further 5 minutes. The prepared substrates were placed in the spin coater and 80 µL of the solution was dropped onto the surface. The solution was spread across the surface and then the spin program was started. The substrate was spun at 4000 rpm for 45 s. The substrates were then left exposed to the air overnight to allow activation of the Spiro layer.

3.5.13 P3HT layer

P3HT (20 mg, Ossila M102) was dissolved in chlorobenzene (1 mL) by stirring and heating to 50 ºC for 10 minutes. A clear, deep red solution was formed, which was filtered using a syringe filter with 0.45 µm pore size. The prepared substrates were placed on a spin coater and 100 µL of the solution was dropped onto the surface. The spin program was started immediately. The substrate was spun at 2000 rpm for 30 s. Once the spin program was complete the substrate was removed and left for 10 minutes for the chlorobenzene to fully evaporate.

3.5.14 Gold layer

A NanoPVD thermal evaporator was used for the deposition of this layer. Gold wire (150 mg, 3N purity) was loaded into the tungsten resistive heating boat and the prepared substrates were loaded into the deposition mask. This mask was designed to pattern the gold layer such that it provided 2 contacts along the edge of the cell for electrical contact to the FTO layer and a further 6 contacts acting as the back electrical contacts of the 6 individual 6.25 mm² solar cell pixels. This arrangement is described in further detail in Section 3.5.1.

The evaporator was sealed and the chamber was evacuated. Once the pressure
reached $1.2 \times 10^{-5}$ Pa the current was switched on. The current was slowly ramped to 90% on the first transformer winding, supplying a current of 55 A. This was held for 1 minute. After this current was increased to 80% on the second transformer winding, supplying a current of 64 A. This was held for a further 5 minutes. The current was then slowly ramped back down and the chamber was vented.

### 3.5.15 MAPbI$_3$ layer

The following procedure was carried out in a dry box filled with dry nitrogen. Methylammonium iodide (199 mg, 1.25 mmol) and lead(II) iodide (576 mg, 1.25 mmol) were added to a mixture of 0.8 mL dimethylformamide (DMF) and 0.2 mL dimethylsulphoxide (DMSO). The mixture was stirred for 15 minutes at 50 $^\circ$C until all of the solid had dissolved. The yellow solution was then filtered using a syringe filter with 0.45 µm pore size. The prepared substrates were placed on the spin coater and 100 µL of the solution was dropped onto the surface. The spin program was started immediately. The substrates were spun at 4000 rpm for 30 seconds. Seven seconds into the spin program 200 µL ethyl acetate was dropped onto the surface. Once the spin program was complete the substrate was placed on a hot plate at 100 $^\circ$C for 30 minutes. A foil lid was placed over the substrates to keep the heat in. Once the annealing step was complete the substrates were allowed to cool to room temperature.

### 3.6 Chapter 6 experimental methods

The following synthetic methods were performed under inert atmosphere (Ar) using a Schlenk line.

#### 3.6.1 Synthesis of [Ca(S₂COEt)$_2$(OHEt)$_3$], Compound 1

A suspension of calcium metal (2.0 g, 50 mmol) in ethanol (100 mL) was stirred and heated under reflux for 4 hours. During this process the metal reacted with the alcohol, forming the soluble metal alkoxide and evolving hydrogen gas. Once the reaction was complete the hazy grey solution was allowed to cool to room temperature. Calcium ethoxide ([Ca(OEt)$_2$(OHEt)$_3$]) precipitated out as a white solid. Carbon disulphide (6 mL, 7.61 g, 100 mmol) was added to the suspension, which began to turn yellow. The precipitate reacted and redissolved, resulting in a hazy yellow solution. The solution was filtered to remove the inert solid. The volume of the solvent was reduced until precipitation occurred. The precipitate was warmed gently back into solution, which was then
cooled to −28°C and left overnight. This results in large yellow crystals. The remaining liquor was extracted and the crystals were dried in *vacuo*. Yield: 19.12 g (91%). (Found: C, 34.09%; H, 6.63%. Calc. for C₁₂H₂₆CaO₅S₄: C, 34.26%; H, 6.71%). NMR δH 1.03 (9 H, t, J = 6.8, CH₃CH₂OH), 1.14 (6 H, t, J = 7.2, CH₃CH₂OCS₂), 2.26 (1 H, br s, CH₃CH₂OH), 3.57 (6 H, q, J = 6.8, CH₃CH₂OH), 4.57 (4 H, q, J = 7.2, CH₃CH₂OCS₂); δC 14.40 (CH₃CH₂OCS₂), 19.80 (CH₃CH₂OH), 59.35 (CH₃CH₂OH), 70.83 (CH₃CH₂OCS₂), 234.11 (CH₃CH₂OCS₂).

3.6.2 Synthesis of [Ca(S₂COEt)₂(pmdeta)], Compound 2

Compound 1 (2.0 g, 4.8 mmol) was dissolved in toluene (20 mL). N, N, N’, N’, N”, N”-pentamethyldiethylenetriamine (pmdeta) (1 mL, 0.83 g, 4.8 mmol) was added and the mixture was stirred overnight. The resulting yellow solution was reduced until precipitation of the product occurred. The solid was warmed back into solution, which was then cooled to −28°C and left overnight. This resulted in yellow crystals forming. The remaining liquor was extracted and the crystals were dried in *vacuo*. Yield: 1.63 g (74%). (Found: C, 38.47%; H, 7.54%; N9.48%. Calc. for C₁₅H₃₃CaN₃O₂S₄: C, 39.53%; H, 7.30%; N, 9.22%). NMR δH 1.10 (6 H, t, J = 7.2, CH₃CH₂OCS₂), 1.46 to 1.53 (2 H, m, pmdeta ethylene backbone), 1.62 to 1.70 (2 H, m, pmdeta ethylene backbone), 1.74 to 1.82 (2 H, m, pmdeta ethylene backbone), 2.08 to 2.21 (12 H + 2 H, m, [(CH₃)₂NCH₂CH₂]₂NCH₃ + pmdeta ethylene backbone), 2.44 (3 H, s, [(CH₃)₂NCH₂CH₂]₂NCH₃), 4.55 (4 H, q, J = 7.2, CH₃CH₂OCS₂); δC 14.60 (CH₃CH₂OCS₂), 44.17 ([(CH₃)₂NCH₂CH₂]₂NCH₃), 46.59 ([(CH₃)₂NCH₂CH₂]₂NCH₃), 55.47 ([(CH₃)₂NCH₂CH₂]₂NCH₃), 57.76 ([(CH₃)₂NCH₂CH₂]₂NCH₃), 69.67 (CH₃CH₂OCS₂), 70.83 (CH₃CH₂OCS₂), 234.11 (CH₃CH₂OCS₂).

3.6.3 Synthesis of [Ca(S₂COEt)₂(py)₃], Compound 3

Compound 1 (2.0 g, 4.8 mmol) was dissolved in toluene (20 mL). Pyridine (1.5 mL) was added to the mixture, which was stirred overnight. The solid dissolved giving a yellow solution. The solvent was removed by evaporation leaving a white solid. Yield: 2.34 g (94%). (Found: C, 48.47%; H, 4.96%; N, 8.15%. Calc. for C₂₁H₂₅CaN₃O₂S₄: C, 48.53%; H, 4.85%; N, 8.08%). NMR δH 1.11 (6 H, t, J = 7.2, CH₃CH₂OH), 4.61 (4 H, q, J = 7.2, CH₃CH₂OH), 6.51 to 6.56 (6 H, m, py C(3)H & C(5)H), 6.78 to 6.85 (3 H, m, py C(4)H), 9.02 to 9.05 (6 H, m, py C(2)H & C(6)H); δC 14.59 (CH₃CH₂OCS₂), 69.73 (CH₃CH₂OCS₂), 124.48 (py C-3 & C-5), 137.46 (py C-4), 150.56 (py C-2 & C-6),
3.6.4 Synthesis of $[\text{Ca}(\text{S}_2\text{COEt})_2(3\text{-mpy})_3]$, Compound 4

Compound 1 (2.0 g, 4.8 mmol) was dissolved in toluene (20 mL). 3-methylpyridine (1.5 mL) was added to the mixture, which was stirred overnight. The solid dissolved to give a yellow solution. The volume of the solvent was reduced to approximately $\frac{2}{3}$ and the solution was cooled to $-28^\circ C$ overnight. Pale yellow crystals had formed, so the liquor was extracted and the crystals were dried in vacuo. Yield: 1.61 g (60%). (Found: C, 51.15%; H, 5.73%; N, 8.15%. Cac. for $\text{C}_{24}\text{H}_{31}\text{CaN}_3\text{O}_2\text{S}_4$: C, 51.31%; H, 5.56%; N, 7.48%). NMR δH 1.12 (6 H, t, $J = 7.2$, CH$_3$CH$_2$OCS$_2$), 1.71 (9 H, s, 3-mpy C(3)Me), 4.61 (4 H, q, $J = 7.2$, CH$_3$CH$_2$OCS$_2$), 6.58 (3 H, m, 3-mpy C(5)H), 6.73 (3 H, m, 3-mpy C(4)H), 8.93 (6 H, m, 3-mpy C(2)H & C(6)H); δC 14.61 (CH$_3$CH$_2$OCS$_2$), 18.40 (3-mpy C(3)Me), 123.88 (3-mpy C(5)H), 134.05 (3-mpy C(3)), 137.76 (3-mpy C(4)), 147.84 (3-mpy C(6)), 151.04 (3-mpy C(2)).

3.6.5 Synthesis of $[\text{Ca}(\text{S}_2\text{COEt})_2(4\text{-mpy})_3]$, Compound 5

Compound 1 (2.0 g, 4.8 mmol) was dissolved in toluene (20 mL). 4-methylpyridine (1.5 mL) was added to the mixture, which was then stirred overnight. The solid dissolved to give a yellow solution. The solution was reduced in volume until precipitation occurred. The solid was warmed back into solution, which was then cooled to $-28^\circ C$ overnight. Pale yellow crystals formed. The liquor was extracted and the crystals were dried in vacuo. Yield: 1.59 g (59%). (Found: C, 52.98%; H, 6.13%; N, 6.39%. Cac. for $\text{C}_{24}\text{H}_{31}\text{CaN}_3\text{O}_2\text{S}_4$: C, 51.31%; H, 5.56%; N, 7.48%). NMR δH 1.15 (6 H, t, $J = 7.2$, CH$_3$CH$_2$OCS$_2$), 1.58 (9 H, s, 4-mpy C(4)Me), 4.66 (4 H, q, $J = 7.2$, CH$_3$CH$_2$OCS$_2$), 6.43 (6 H, dd, $J_1 = 1.8$, $J_2 = 4.8$, 4-mpy C(3)H & C(5)H), 9.00 (6 H, dd, $J_1 = 1.8$, $J_2 = 4.8$, 4-mpy C(2)H & C(6)H); δC 14.65 (CH$_3$CH$_2$OCS$_2$), 125.41 (4-mpy C-3 & C-5), 148.95 (4-mpy C-4), 150.34 (4-mpy C-2 & C-6). The signal for CH$_3$CH$_2$OCS$_2$ was not seen.

3.6.6 Synthesis of $[\text{Ca}(\text{S}_2\text{COEt})_2(4\text{-dmap})_3]$, Compound 6

Compound 1 (2.0 g, 4.8 mmol) and 4-dimethylaminopyridine (4-dmap) (1.74 g, 14.2 mmol) was added to toluene (20 mL). The mixture was gently heated with stirring until all of the solid had dissolved, giving a yellow solution. The solution was allowed to cool to room temperature, whereupon crystals began to grow. The solution was then fur-
her cooled to $-28^\circ$C overnight. The liquor was extracted and the crystals were dried in vacuo. Yield: 2.06 g (66%). (Found: C, 49.95%; H, 6.49%; N, 10.19%. Calc. for C$_{27}$H$_{40}$CaN$_6$O$_2$S$_4$: C, 49.97%; H, 6.21%; N, 12.95%). NMR $^\delta$H 1.21 (6 H, t, $J = 7.2$, CH$_3$CH$_2$OCS$_2$), 2.08 (18 H, s, 4-dmap C(4)NMe$_2$), 4.76 (4 H, q, $J = 7.2$, CH$_3$CH$_2$OCS$_2$), 5.88 (6 H, dd, $J_1 = 1.7$, $J_2 = 5.3$, 4-dmap C(3)H & C(5)H), 8.92 (6 H, dd, $J_1 = 1.7$, $J_2 = 5.3$, 4-dmap C(2)H & C(6)H); $^\delta$C 14.83 (CH$_3$CH$_2$OCS$_2$), 38.49 (4-dmap C(4)NMe$_2$), 69.16 (CH$_3$CH$_2$OCS$_2$), 106.98 (4-dmap C-3 & C-5), 150.68 (4-dmap C-2 & C-6), 154.78 (4-dmap C-4). The signal for CH$_3$CH$_2$OCS$_2$ was not seen.

3.6.7 Aerosol-assisted chemical vapour deposition using calcium xanthate precursors

This is a general overview of the procedure carried out for AACVD using the calcium xanthate precursors (Compounds 1 to 6). Specific parameters are given in the discussion in Chapter 6.

100 mL carrier solvent was measured into a conical flask, to which the solid precursor was added to form a 0.1 M solution. The solid dissolved easily, so the mixture was agitated until a clear yellow solution was formed. The solution was poured into a stainless steel bubbler, which was then closed and sealed.

In the meantime the substrates were prepared. The substrates used in this chapter were float glass and silicon wafer. These substrates were cleaned by the procedures detailed in Sections 3.1.2 and 3.1.3.

The bubbler was attached to the nebuliser and the substrates were placed on a glass sheet which slid into place inside the reactor tube to direct the flow of the aerosol over the substrates. The reactor tube was slid into a tube furnace so that the substrates were in the middle of the furnace.

Once this was complete the system was sealed. A flow of nitrogen gas was introduced through the nebuliser and the furnace was switched on. The system was left in this state for 30 minutes to allow for residual air to be removed from the system and for the temperature to stabilise at the desired value.

Once this time had elapsed, the valves to the bubbler were opened which allowed the precursor to be drawn up to the nebuliser and turned into an aerosol on contact with the gas stream, as explained in Section 1.2. The deposition was run until all of the precursor solution had been used up. The rate at which this occurred was dependent upon the flow rate of the carrier gas.
Once the precursor solution had been used up the furnace was switched off and the system was left to cool to room temperature with the flow of nitrogen gas through the reaction tube.

References


Chapter 4

Deposition of tin(II) sulphide from tin(II) ethylxanthate

4.1 Introduction

Tin(II) sulphide (SnS) is a naturally occurring compound also known as the mineral hertzenbergite. Like many of the metal sulphides it has a band gap that is small enough to allow some electrical conduction and its resistance decreases as its temperature increases. SnS is intrinsically a p-type semiconductor due to the defects which naturally become incorporated into the crystal structure as it forms. It has been shown however that aliovalent substitution\(^1\) of Cl\(^-\) for S\(^{2-}\) above the level of 0.5% results in carrier type conversion and the SnS becomes an n-type semiconductor.\(^2,3\)

Hertzenbergite (also known as \(\alpha\)-SnS) is the most common form of SnS. This phase has an orthorhombic structure involving sheets of tin and sulphur atoms separated by

Figure 4-1: A representation of the crystal structure of \(\alpha\)-SnS (hertzenbergite).
voids in which the lone pairs of the tin atoms sit (see Figure 4-1). The layered structure of this material makes it electronically anisotropic. Along the \( a \) and \( b \) axes (parallel to the layers) the effective mass of the minority carriers is relatively low (0.2 \( m_0 \)). In the \( c \) axis however (transverse to the layers), the effective mass is considerably higher (0.5 \( m_0 \)).\(^4\) This has the effect of reducing the carrier mobility by between three and six\(^5\) times in the \( c \) direction. For the purposes of a thin film solar cell this is a drawback. In a multicrystalline thin-film the random orientation of the crystallites in the film means some crystals will be sitting in an orientation which will slow the flow of carriers through the film.

Despite the electronic anisotropy, \( \alpha \)-SnS has numerous properties that make it desirable as a photovoltaic material. First of all its constituent parts (i.e. tin and sulphur) are relatively earth abundant\(^6\) and already extracted on a large scale meaning that the material is relatively cheap to produce. It has both an indirect and a direct band gap, with ranges of 1.0 eV to 1.25 eV\(^1,5,7-13\) and 1.20 eV to 1.43 eV\(^3,14-22\) respectively. These values are very close to the ideal band gap for a photovoltaic absorber material, as stated in Section 2.5. Reports of the absorption coefficient\(^23-32\) are in the range of \( 10^4 \) cm\(^{-1}\) to \( 10^6 \) cm\(^{-1}\). Majority carrier concentrations\(^4,5,33-39\) of \( 10^{15} \) cm\(^{-3}\) to \( 10^{18} \) cm\(^{-3}\) and carrier mobilities\(^40-47\) of 0.6 cm\(^2\) V s\(^{-1}\) to 128 cm\(^2\) V s\(^{-1}\) have also been reported. For all of these properties a range has been given because the exact values for a particular film are highly dependent upon the way the film was made.

Thanks to its electronic properties \( \alpha \)-SnS is also of interest in a variety of other applications. Its ability to strongly absorb incident light has made it useful as a highly responsive photodetector.\(^48-50\) Its sensing ability is not limited to light however: a report by Naghian et al. demonstrates its use as a sensor for soluble molecules such as paracetamol and hydroquinone.\(^51\) In addition, SnS also exhibits thermoelectric properties and its potential as a thermoelectric generator has also been studied.\(^52\)

While the structure of \( \alpha \)-SnS is not ideal for photovoltaics, it is a potentially desirable quality in battery storage technologies. The layered arrangement of its atoms potentially makes it very well suited for the storage of ions and its theoretical energy capacity is very high. For this reason, \( \alpha \)-SnS has been investigated extensively as an anode material in both Li-\(^53,54\) and Na-based\(^55,56\) battery technologies.
4.1.1 Tin(II) sulphide and polymorphism

Like many tin-containing compounds, tin(II) sulphide is a polymorphic material. This means that it can exist in a variety of different phases depending upon the conditions in which it was made. In 1968 another polymorph of SnS was found by epitaxial deposition onto the (100) face of a NaCl substrate at temperatures above 770 K. This phase echoed the cubic structure of the NaCl substrate, was apparently stable at room temperature and had a band gap of 1.2 eV.

Cubic crystals are structurally isotropic, their properties appearing identical regardless of the frame of reference. Without the weakly bound layers there is nothing to impede the movement of charge carriers in the $c$ direction, meaning that this phase is electronically isotropic too. As a result a polycrystalline film of cubic SnS would theoretically have a lower resistance to the flow of carriers that one made from orthorhombic SnS and so should be superior as a photovoltaic absorber layer.

Another report by Vidal et al. described a method by which the rock-salt phase could be deposited onto a silicon substrate by pulsed laser deposition (PLD) with substrate temperatures between 300°C and 600°C. This was done by co-depositing SnS with group 2 metal sulphides, namely MgS, CaS and SrS. Not only did the inclusion of these compounds stabilise the cubic structure, the absorption onset of the material was seen to be much steeper in the CaS and SrS alloys. The band gap itself was tunable between 25% and 50% alloyed sulphide, giving a range of band gap values from 0.6 eV to 1.5 eV.
In 2006 another phase of SnS was identified in SnS nano- and microcrystals synthesised by reaction of tin(II) chloride and elemental sulphur in the presence of oleylamine at 170°C. The new phase also had a cubic structure and was attributed to the zinc blende structural family due to the ratios of particular peak intensities matching those of the zinc blende structure most closely. However, the zinc blende structure could not account for all of the peaks seen in the pattern of this new phase. The authors theorised that the other peaks were the result of preferential orientation, other tin sulphide phases or even other materials.

A pseudo-tetragonal structure was put forward by Biacchi et al. which accounted for some of the extra peaks. The structure could not however account for the cubic phase’s most prominent feature: the triple peaks seen at $2\theta = 31.0^\circ, 31.9^\circ$ and $32.9^\circ$.

Further evidence came in the form of computational modelling of the proposed zinc blende SnS structure, which suggested that it was unstable even at room temperature. This led the authors of the computational report to suggest that the zinc blende assignment was incorrect. Rabkin et al. studied the powder electron diffraction patterns from nanocrystals of the cubic SnS and constructed Bärnighausen trees for the relationship of the observed structure with both the zinc blende and rock salt theoretical structures. This is a method by which the relationship between different crystal structures can be determined through analysis of their symmetry. It can be used to determine the crystalline symmetry subgroup to which a particular structure belongs. In this case the authors successfully constructed a Bärnighausen tree linking the rock salt structure to the observed structure, but when starting from the zinc blende structure the observed structure could not be linked.

Rabkin et al. concluded by proposing the now accepted form of cubic SnS: a simple cubic unit cell containing 64 atoms. They also gave the phase a name: $\pi$-SnS. This new structure accounted for both the electron diffraction patterns as well as all of the X-ray diffraction peaks. The matter was finally put to rest when the previously discussed “cubic SnS” and the newly proposed “$\pi$-SnS” were shown to be one and the same.

4.1.2 Optical properties of $\pi$-SnS

As described in Section 2.6.1, the most accurate way to estimate the optical band gap is to use the Tauc transformation. The value of $r$ in the Tauc transformation $(\alpha h\nu)^1/2$ is dependent upon the type of transition which is occurring.

It is unclear from the literature what type of transition is dominant in the $\pi$-SnS
system. The first paper to report $\pi$-SnS performed optical measurements on their crystallites, noting the presence of a strong absorption edge and a “gradual rise” at larger wavelengths.\textsuperscript{13} No attempt was made to assign these features.

Of the papers which perform analysis on the absorption spectrum of the material using the Tauc transformation, many suggest that the transition is direct forbidden\textsuperscript{58,59,67-69} with a band gap of 1.66 eV to 1.75 eV, however this does not make sense for a material with an absorption coefficient of more than $10^4 \text{cm}^{-1}$. Forbidden transitions are discussed in detail in Section 2.5. In brief, a forbidden transition violates the Laporte selection rule, meaning that it can only occur if the rule is relaxed. This happens due to vibrational distortion of the crystal structure, momentarily destroying orbital symmetry and making the transition “partially allowed.” As this is a transitory occurrence the absorption due to forbidden transitions is significantly weaker than allowed transitions, often by as much as three orders of magnitude.\textsuperscript{70}

This is not to say that the material does not possess a forbidden transition. Depending on their band structure materials can have a variety of different potential electronic transitions, however with a highly absorbing semiconductor the transition of interest is the one that gives rise to the band edge seen in optical measurements. This is the photon energy above which the material becomes strongly absorbing.

The report by Abutbul et al. goes into greater detail stating that due to the crystal’s small Brillouin zone (a result of its large unit cell), they were unable to calculate whether or not the band gap was indirect.\textsuperscript{9} Despite this, Abutbul et al. have used the value of $r = 2$ for analysis of both $\alpha$-SnS and $\pi$-SnS. They justify this with the observation that when analysing the $\pi$ phase in a manner similar to the $\alpha$ phase, the resulting Tauc plot yields a linear portion, indicating that the $\pi$ phase also possesses an indirect allowed band gap. This is backed up by predictions made by Greyson et al.,\textsuperscript{13} and yielded a value for the band gap of 1.53 eV.

Where specified, the reports mentioned in this section attribute their selection of the value of $r$ and thus the type of transition to whichever plot gave the expected linear region from which a value for the band gap could be determined.

### 4.1.3 Deposition of tin(II) sulphide

As interest in SnS in its various forms has grown, a wide variety of different techniques have been used to deposit it. In many cases the method used to synthesise the material reflects the focus of the work. Studies which probed the properties and application
of thin films of SnS used techniques such as thermal evaporation, PLD, sintering, electrodeposition, sputtering, CVD, AACVD, spray pyrolysis, spin coating, chemical bath deposition (CBD), molecular beam epitaxy (MBE) and atomic layer deposition (ALD). Most reports centred around the use of nanoparticulate SnS used solvothermal synthesis to generate their nanoparticles, however successive layer adsorption and reaction (SILAR) and liquid-phase exfoliation have also been used.

A variety of single-source precursors have been put forward for the deposition of SnS including dithiocarbamates, guanidinates, thio carb oxylates and thioureates. All of these compounds have required relatively high temperatures (>300 °C) to achieve successful deposition and many are significantly air sensitive, which adds to the complexity of their handling and use.

The aim of this section of work was to develop a suitable precursor for the deposition of tin monosulphide (SnS) by aerosol-assisted chemical vapour deposition due to the scalability, reproducibility and relatively low complexity of this deposition technique. Tin(II) ethylixanthate was considered to be a good candidate for this study. As stated earlier, metal xanthates have been used widely to deposit a range of metal sulphides and are known for their ability to decompose cleanly at comparatively low temperatures to form the corresponding metal sulphide.

Tin(II) ethylixanthate has previously been used for the synthesis of tin sulphide nanoparticles via solvothermal synthesis. The reaction temperature was very low (180 °C to 240 °C) and by modifying the reaction conditions both α- and π-SnS nanoparticles could be synthesised in a controlled manner.

There is one report in the literature in which tin(II) xanthate has been used as a precursor for AACVD, however only a single set of experimental conditions is reported, using a deposition temperature of 300 °C. The experiment was unsuccessful, resulting in an amorphous film which was seen to contain tin and sulphur, but which was too thin to give quantitative data. The authors note that when decomposed under solvothermal conditions, hexagonal nanoparticles of SnS were formed.

4.2 Synthetic methods and characterisation

As described in Section 3.4 the tin ethylixanthate precursor prepared for this work was synthesised by two different methods. The first followed a preparation reported by
Kociok-Köhn et al. wherein the reagents were first dissolved or dispersed in water, then mixed slowly to allow reaction to occur. The resultant pale yellow solid produced by this method contained a large amount potassium chloride (the byproduct of the salt metathesis reaction) and so needed to be purified. Recrystallisation was attempted from methanol (as directed by the paper), THF, ethanol, isopropanol, hexane, toluene and diethyl ether, however in every case the result was thick orange oil which when analysed appeared to be predominantly dixanthogen. Attempts were made instead to simply wash the solid with copious amounts of water in an attempt to dissolve away the remaining salt, but this was unsuccessful and use of the resulting precursor sometimes led to chlorine contamination of the film.

The second method attempted to make the compound anhydrously. The same solids were this time dispersed in dry, degassed THF in separate Schlenk flasks under an inert atmosphere. The solution of SnCl$_2$ was then transferred to the other Schlenk flask by cannula. The mixture turned a pale yellow as the product was produced and the salt by-product precipitated as a fine white powder. This precipitate had to be filtered out of the solution using a sintered glass filter stick, but once this was done the resulting precursor had a high purity.

It quickly became apparent that the product was quite temperature sensitive, showing a gradual colour change from pale yellow to orange at room temperature over the course of many hours. After a couple of weeks the compound became black. The problem of temperature sensitivity was further exacerbated by the fact that the reaction of the SnCl$_2$ and KS$_2$COEt is significantly exothermic. To get around these problems the vessels containing the reagent solutions were immersed in an ice bath during the course of the reaction and mixing was done slowly and carefully to allow time for the heat generated to be dissipated. The product was found to remain stable if kept under vacuum, or at $-28^\circ$C.

NMR spectroscopy of material made by the two different methods gave almost identical results. The only difference that was seen was the intensity of a number of very small triplets and quartets seen in the $^1$H NMR spectra. While these extra peaks were extremely low in intensity, they appeared to have a slightly higher intensity in the compound made by the water method. NMR spectra of the compounds can be found in Appendix B.

Thermo-gravimetric analysis of the compound shows a single, sharp decomposition step with an onset of 91 $^\circ$C and an endpoint of 126 $^\circ$C. The TGA trace of this compound
is shown in Figure 4-3. After this step, the mass stabilised and remained unchanged for the remainder of the experiment, indicating that the residual material was thermally stable up to a temperature of 500 °C.

The residual mass after decomposition of the compound was calculated to be 43.4% of the starting mass. Based on the relative molecular masses of Sn(S₂COEt)₂ and SnS, if the compound had decomposed cleanly to form SnS the residual mass would be expected to be 41.8%. The discrepancy between these two values is very small, and can most likely be attributed to experimental error. A higher residual mass than expected can indicate that complete decomposition has not been achieved and that some extra residue is present in the films. Another possibility is that a small amount of the precursor had begun to decompose during storage and transport, resulting in the initial mass being lower than that which would be expected for the pure precursor.

4.3 Deposition of films from tin ethyl xanthate by AACVD

AACVD was used to deposit suitable samples for characterisation of the decomposition product. A general description of the technique was given in Section 3.4.3. For this deposition Sn(S₂COEt)₂ (1.8 g, 5 mmol) was dissolved in 50 mL THF to produce a 0.1 M solution. A range of deposition temperatures from 125 °C to 300 °C were attempted.

A combination of powder x-ray diffraction (PXRD), energy-dispersive x-ray
spectroscopy (EDXS) and Raman spectroscopy were used to characterise the product. EDXS is a quantitative technique, capable of giving the elemental composition of a sample in terms of a numerical ratio. PXRD on the other hand is mainly a qualitative technique, capable of giving information on the identity of crystalline phases in the sample. Crucially, materials will only be identifiable if they are crystalline: an amorphous phase will not give any identifiable response in the PXRD pattern.

Raman spectroscopy is also qualitative, giving a specific pattern of peaks for a specific material. Amorphous material will not show up on a Raman spectrum either, but due to the fact that it uses visible light rather than x-rays, Raman is a considerably more surface-sensitive technique. The technique works by the interaction of light with certain vibrational modes in the analysed material. For a vibrational mode to be "Raman active", the vibration must be accompanied by a change in the polarisability of the molecular structure. Some materials do not have any vibrational modes which exhibit a change in polarisability and so are completely Raman inactive and cannot be seen by the technique regardless of their crystallinity.

Below 150 °C and above 250 °C very little deposition was seen on the substrate and no PXRD pattern or Raman signal could be collected from the deposited films. Between these temperatures a glossy brown/black film was deposited. PXRD and Raman of the deposited films is shown in Figure 4-4. No background correction was used in the processing of these data due to the low intensity of the signals and broad, poorly defined peaks. The narrow peak at 33.2° is a signal from the silicon substrate (as seen in the pattern from the blank Si wafer in Figure 4-4a) and is used as an internal standard to correct for instrumental error in the peak positions. This corresponds to the (201) peak of the JCPDS PDF #40-0932 silicon pattern.

All three patterns show signals of extremely low intensity, as evidenced by the very poor signal to noise ratio. The patterns each exhibit two or three very broad peaks, none of which could be successfully assigned. The film deposited at 250 °C also showed two smaller, narrower peaks at 28.7° and 31.6°. The larger peak coincides with the principal peak of the α-SnS pattern, however no other evidence of the α-SnS pattern could be found. The smaller peak could not be successfully assigned.

While very little information can be gained from the films’ diffractograms there is some useful information contained in the Raman spectra. All three spectra show a peak at approximately 109 cm⁻¹ which corresponds to the B_{1g} mode of SnO. This is the most intense peak in all three spectra. The spectra at 150 °C and 250 °C also show a
Figure 4-4: PXRD patterns (a) and Raman spectra (b) of films deposited from Sn(S$_2$COEt)$_2$ at 150, 200 and 250°C.

A peak at around 219 cm$^{-1}$ which matches one of the A$_g$ modes in $\alpha$-SnS. These are not definitive proof of the existence of these materials in the films as no other peaks from the spectra of either of these compounds is seen, but it does potentially give an idea of the film composition. As both techniques show indications that SnS may be present, this increases the likelihood that this is a positive reading.

EDXS measurements for the film deposited at 250°C are given in Table 4.1. Measurements of the other films are not included as they did not show any significant difference from this film. The levels of Sn in the film are roughly 50%, meaning that the stoichiometry of cations to anions is approximately 1:1 and, making the assumption that the sulphur exists as a 2- anion, the majority of the tin is likely to be in the 2+ oxidation state. The other 50% of the film is a mixture of oxygen and sulphur in roughly a 3:1 ratio. The presence of significant levels of oxygen and the ratios of tin to chalcogenides corroborates the indications from Raman and PXRD that the principal component of the film is SnO with a smaller amount of SnS, however due to the lack of signals in both of these sets of data it is likely that much of the material is amorphous.
<table>
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<th>Measurement</th>
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<td>12.15</td>
<td>37.26</td>
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</table>

**Average** 53.43 11.55 35.02

Table 4.1: EDXS measurements of the film deposited from Sn(S₂COEt)₂ at 250°C. Si signal omitted for clarity.

### 4.4 Exclusion of oxygen from deposited films

There are a number of possible sources for the oxygen present in the films. Each step of the procedure was analysed for the potential to introduce oxygen into the system. A new batch of precursor was synthesised using anhydrous solvents and reagents and Schlenk line techniques as described in the anhydrous method in Section 3.4. Once dry the solid was collected in a glove box.

Dry, distilled THF was degassed twice for use as the carrier solvent. The solution was made up, loaded into the bubbler and sealed in a glove box. The entire AACVD system was cleaned thoroughly, checked for leaks and was purged for an hour with nitrogen gas before the deposition was started. The temperature was set at 200°C.

Figure 4-5 shows the PXRD pattern and Raman spectrum collected from the deposited film. Once again the signals seen in the data are extremely low intensity (the area under the peak is small), however this time there are identifiable peaks present.

Both plots exhibit signals that match multiple different materials and many of the peaks present in both sets of data could be ascribed to two or more materials. Determining the composition of a potential mixture of SnS, SnO, SnS₂, SnO₂ and Sn₂S₃ by PXRD or Raman can be very challenging because these compounds all have a number of peaks in very similar areas. This is further exacerbated by the fact that PXRD patterns of thin films often do not display the full set of peaks seen in the pattern of the bulk material and can often have very different relative peak intensities too. Using a combination of PXRD, Raman and EDXS together can help form a much more accurate
Figure 4-5: PXRD pattern (a) and Raman spectrum (b) of a film deposited by AACVD from Sn(S_2COEt)_2.

picture of the material(s) present in the sample.

The references shown in Table 4.2 were compared to the experimental data. A process of elimination was used to find the most likely set of materials which would provide the patterns seen in both plots. A combination of SnO, Sn_2S_3 and α-SnS satisfies the set of signals seen, however a number of characteristic signals for the potential materials were missing. Considering the low intensity of the signal this is not too surprising, however because of the uncertainty involved these assignments are tentative.

When compared to the silicon PXRD peak the other peaks in the PXRD data are considerably more broad. There are a number of factors which may affect the width of PXRD peaks. Heterogeneity of the sample is one such factor and this is likely to be responsible for some of the peak broadening seen here. Without information on

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<th>Raman reference</th>
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<td>Chandrasekhar 1977^100, Abutbul 2016^9</td>
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<td>Ahmet 2015,^83 Abutbul 2016^9,^64</td>
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<td>Steichen 2013,^11 Skelton 2017^102</td>
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<td>PDF #21-1231</td>
<td>Mead 1976^103</td>
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Table 4.2: References used for PXRD and Raman peak comparisons.
properties of the film such as crystallite size, strain and lattice imperfections however it is impossible to determine how much of the peak broadening is a result of each of these effects.

EDXS (shown in Table 4.3) provides further evidence for the assignments proposed above. Surprisingly, after eliminating all potential sources of oxygen contamination, the ratio of oxygen to sulphur is even higher than in the previous set of samples. Combining this finding with those from PXRD and Raman a picture of the morphology of the film emerges.

The ratio of metal to chalcogenide is again close to 1:1, indicating that on the whole the tin is in the 2+ oxidation state. This is of course with exception to the apparent presence of a small amount of Sn$_2$S$_3$ which may explain the presence of the slight atomic excess of tin. Despite the large proportion of oxide present in the film, the area under the peaks corresponding to SnO are relatively small. This may indicate that much of the oxide is not crystalline. Based on this information the film appears to consist of a mostly amorphous matrix of tin monoxide with small crystallites of α-SnS and Sn$_2$S$_3$ suspended within it.

<table>
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Table 4.3: EDXS measurements of film deposited from Sn(S$_2$COEt)$_2$ anhydrously at 200 °C. Si signal omitted for clarity.
4.5 Investigation of decomposition mechanism

Having eliminated all other potential sources of oxygen from the deposition process the only remaining source is the xanthate ligand itself. This is highly unexpected as it entirely contradicts the findings from analysis of the residual mass in the TGA experiment. In the TGA analysis the residual mass was reasonably close to what would be expected for SnS and was in fact slightly higher than expected. Measurements of deposited films on the other hand indicate the major component to be SnO, which would be expected to have a lower residual mass. The presence of large amounts of contaminants can be ruled out as these would be seen by EDXS in the deposited films. Furthermore, if the contamination was a result of incomplete decomposition during TGA, further breakdown of the intermediate components would be expected at higher temperatures.

This leads to the idea that the material’s decomposition behaviour during the TGA experiment is entirely different from its behaviour during AACVD. Based on the literature concerning metal xanthates as precursors (discussed in Section 1.3), the formation of metal oxide is highly unusual, but the precedent for such a process does exist. This would suggest that the dominant decomposition mechanism for tin(II) xanthate is different from the mechanisms described for other studied metal xanthates.

While it may not be entirely representative of the decomposition pathway followed during AACVD to form metal oxide films, study of the decomposition during heating of the solid (as occurs in TGA) at least allows the precursor to be compared to those in literature. Concurrent thermo-gravimetric and mass spectrum analysis (TGA-MS) was performed on the compound to attempt to understand the decomposition process. In this technique the sample undergoes standard thermo-gravimetric analysis, but rather than the exhaust gases being vented they are transferred to a gas-phase mass spectrum (MS) analyser. In this way, the various gaseous by-products of the decomposition can be identified and linked to the stage of the deposition process in which they were released.

Figure 4-6 shows the results of this analysis. The MS was configured to sweep the entire range of fragment masses that it could detect. The heat map represents the data collected from the MS. Coloured areas represent a signal detected for a particular fragment mass at a particular time. The stronger the colour, the more intense the signal detected.

Overlaid on this plot is the associated TGA trace for this measurement. With this information signals in the MS data associated with byproducts of the decomposition
reaction can easily be identified. At some of the lower m/z values a current is detected for the entirety of measurement. These values correspond to common fragments of species found in the air and the blanket gas used for the TGA experiment.

There is a significant amount of information contained in the mass spectra collected during this experiment. Signals are not only detected for the molecular ions of the byproducts coming off the reaction, but also for a host of fragments and secondary species created in the process of ionising the molecules which enter the MS. In the case of volatile molecules a mass spectrum will exhibit a fingerprint pattern of peaks which may be used to identify the original material based on the manner in which it fragments.

When it comes to analysing decomposition products the deconvolution of a particular species’ fingerprint pattern from those of all the other decomposition products is extremely challenging. In circumstances where multiple species exist one solution is to analyse control samples of the various suspected fragments. This allows the identification of the specific pattern and ratios of peaks produced by that species in the mass spectrum analyser. The results of the control samples can then be compared to the spectrum in question to identify whether or not the suspected species are present.

Unfortunately in this case this method was not feasible due to the large number of
potential species and the propensity for the formation of highly reactive species that could go on to modify other species, further complicating the spectrum. Instead, the presence or absence of the molecular ion and its related signals is examined. This means that while suggestions can be made for which fragments might be present, the presence or absence of a particular species cannot be fully verified. It is also important to note that some signals may not be due to the generation of the species suggested during primary decomposition and could instead be caused by the fragmentation of larger species during ionisation. This is particularly important for smaller m/z values.

The blanket gas used in this experiment was argon, hence the very strong consistent signal at m/z = 40, as well as lesser signals at m/z = 20 (Ar\(^{2+}\)) and 80 (Ar\(^{2+}\)) amongst others. As well as the argon signals, there are a number of other m/z values for which an appreciable signal is detected throughout the experiment. These signals are due to atoms or compounds that are present either in the blanket gas or in the small amounts of air which are able to enter the system. The species responsible have low masses, generally <40 Da, and so make it difficult to detect species of low mass generated in the decomposition of the sample.

Interestingly, while no rational decomposition species could be found with a m/z value of 40 a peak was still seen in the spectrum coinciding with the decomposition as detected by TGA. This can be seen in Figure 4-7. This could not be the result of a doubly-ionised fragment of mass 80 as the signal at m/z = 80 is much too weak. The same phenomenon was also seen in the other residual gas signals. Some of these peaks could be attributed to low mass species being generated in the decomposition of the sample. Others however, like the m/z = 40 signal, could not be assigned to a rational fragment of the sample.

One potential explanation for this effect may be that as the precursor decomposes it generates additional gases which affect the pressure and gas flow within the furnace. This changes the conditions under which species are entering the MS, causing a fluctuation in the signal. This then raises the question of whether the peaks seen in the atmospheric signals are due to evolution of species with the same mass, or whether they are an artefact of the changing conditions in the gas flow.

In order to answer this question, the contribution to the peak caused by the change in gas flow must be determined. As the argon signal at m/z = 40 has a very high signal to noise ratio and cannot be linked to any other potential fragment, this was chosen to represent the effect of the change in gas flow.
To proceed with this analysis two assumptions must be made. Firstly, all m/z values and the fragments which cause them must be affected equally by the change in gas flow, i.e. the strength of the response must be independent of the mass or geometry of the fragment. Secondly, the magnitude of the response must be proportional to the concentration of fragments with a particular mass. In other words, the integral of the peak resulting from a change in gas flow must be proportional to the integral of the background of that signal. With this established, the peak integral was divided by the baseline integral to determine a concentration-independent ratio for the peak intensity. In the case of the m/z = 40 signal, this value was 0.18.

If the assumptions made above are correct, comparing this value to the same value calculated for other signals will give an indication of whether or not the peak in the other signals is a result of fragments of that mass being formed. If the value is approximately 0.18, there are no extra fragments contributing to the peak. A value significantly greater than 0.18 (e.g. an order of magnitude greater or more) suggests that fragments of that mass are being generated as a result of the decomposition.

Where possible, quantitative analysis was performed on the signals in order to determine whether peaks were linked by isotopic ratio. This was done by background subtraction of the signal so that the integral of the peak could be determined. The integrals of the peaks were then compared to one another to see if their relative magnitudes echoed the isotopic ratios expected. If a set of signals had peaks whose intensity ratios matched the natural abundances of the elements present in a proposed fragment, this provides compelling evidence that the proposed fragment is responsible for the peaks.
In the vast majority of cases the ratios did not match. This is most likely caused by the presence of other species with the same m/z values, which will distort the ratios of peak intensities.

Table 4.4 gives species associated with the proposed decomposition mechanisms discussed in Section 1.3.2. All m/z values presented in this table show a signal with a clear peak which coincides with the decomposition step seen in the TGA trace. The only compound mentioned in the literature for which no potential molecular ion was seen was EtOCSMe (molecular ion m/z: 104).

As has been seen repeatedly in other studies of xanthates the major decomposition products appear to be CS$_2$ and COS. Ignoring the signals for atmospheric gases, m/z = 60 (COS) and 76 (CS$_2$) are the most intense peaks seen in this experiment. The evidence for these two compounds is strong as the peak ratios for the molecular ion, M+1 and M+2 species matched those of the isotopic ratio with reasonable accuracy.

Vreugdenhil et al. also report CO$_2$ and CO as major products of the decomposition. In this experiment CO$_2$ present in the air during loading of the sample leads to a residual signal throughout the course of the measurements, however the ratio of the peak height to the baseline is approximately 36 (compared to 0.18 for argon as mentioned earlier). This would suggest that while some CO$_2$ is present as residual atmospheric gas, the decomposition of the precursor is also generating CO$_2$ and/or another species with a mass of 44.

CO has the same mass as N$_2$, which again is present in the residual atmospheric gases. This meant that a positive match for CO could not be determined. Furthermore the corresponding peak ratio at m/z = 28 was only 0.24 and so should be ignored. This is likely due to the high concentration of N$_2$ drowning out the weaker signal of other species which may be produced here. That being said, the peak to baseline ratios of the signals at m/z = 29 and 30 are 3.6 and 5.1 respectively, indicating that something is possibly being produced with these masses. These masses correspond to the M+1 and M+2 isotopes of CO, although as mentioned earlier they could also be the result of doubly ionised species of mass 58 and 60 Da. The signal at m/z = 60 is much more intense than the one at m/z = 30 so this may well be a major factor, however the signal at m/z = 58 is significantly weaker than m/z = 29, so a doubly ionised species is unlikely and CO appears to be the most likely cause of these peaks.

Analysis of the peak intensities for signals at m/z = 44, 60 and 76 reveals that the ratio of CS$_2$ to COS is almost equal (I$_{CS_2}$/I$_{COS}$ = 1.08), while the intensity of the peak
<table>
<thead>
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<th>m/z</th>
<th>Species</th>
<th>m/z</th>
<th>Species</th>
</tr>
</thead>
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<tr>
<td>28</td>
<td>C₂H₄, CO</td>
<td>29</td>
<td>C₂H₄ M+1, CO M+1</td>
</tr>
<tr>
<td>34</td>
<td>H₂S</td>
<td>36</td>
<td>H₂S M+2</td>
</tr>
<tr>
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<td>CO₂ M+1, CH₃CHO M+1</td>
</tr>
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<td>46</td>
<td>EtOH</td>
<td>47</td>
<td>EtOH M+1</td>
</tr>
<tr>
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<td>SCO M+1</td>
</tr>
<tr>
<td>62</td>
<td>SCO M+2</td>
<td>64</td>
<td>SO₂, S₂</td>
</tr>
<tr>
<td>66</td>
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<td>70</td>
<td>(C₂H₃)₂O</td>
</tr>
<tr>
<td>72</td>
<td>EtOC₂H₃</td>
<td>73</td>
<td>EtOC₂H₃ M+1</td>
</tr>
<tr>
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<td>Et₂O</td>
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</tr>
<tr>
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<td>78</td>
<td>CS₂ M+2, EtSMe M+2</td>
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<td>C₄H₄S M+1</td>
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<td>124</td>
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<td>134</td>
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</tbody>
</table>

Table 4.4: m/z signals in the decomposition of Sn(S₂COEt)₂ which were observed to have a “significant” peak intensity (i.e. peak/background integral ratio > 1.8).

Scheme 4-8: Mechanism for the production of CO₂ during the decomposition of metal xanthates as described by Vreugdenhul et al.¹⁰⁶
at m/z = 44 is over twice as great as either of the other two. This is a surprising result as according to Vreugdenhil et al. the production of CO$_2$ requires first the deinsertion of CS$_2$ from one molecule, rearrangement of and subsequent COS deinsertion from a second molecule, reinsertion of COS into the M-O bond of the first molecule and then transfer of the alkyl group from the oxygen atom to the sulphur to result in release of CO$_2$. A simplified version of this process is shown in Scheme 4-8.

The evidence of the experiment does not support the peak at m/z = 44 being a result of CO$_2$ production by this mechanism. As this mechanism is reliant upon the production of CS$_2$ and COS, the amount of CO$_2$ produced during the reaction could not feasibly exceed the amount of the other two triatomic gases. Furthermore, the large number of steps involved makes it much less likely.

Having established this, another explanation for the strong signal at m/z = 44 is required. The literature provides another candidate fragment for this mass in the form of ethanal.$^{107,108}$ In both of these references, ethanal was identified as a minor decomposition product but no explanation was given for its formation. The most likely explanation seems to be the dehydrogenation of ethanol (also seen as a minor decomposition product), possibly catalysed by the metal oxide or metal sulphide. Some examples of alcohol dehydrogenation by tin oxide containing catalysts do exist,$^{112,113}$ although admittedly nothing specifically for tin monoxide or monosulphide. This conversion would also need to be quite efficient because the peak corresponding to ethanal is two orders of magnitude higher than that of ethanol.

Unfortunately the ratios of m/z = 44, 45 and 46 did not match the isotopic ratio of either of the compounds mentioned above and so a positive identification cannot be made. This may be in part due to both compounds being present as well as the overlap of signals from other decomposition products and their related fragments.

The two species considered to be the most convincing evidence of the Chugaev elimination mechanism discussed in Section 1.3 are ethene and H$_2$S. Unfortunately ethene also has a mass of 28 Da and so no conclusion can be drawn about its presence. H$_2$S has a mass of 34 Da and so peaks would be expected at m/z = 34 and 36 for the molecular ion and M+2 isotopic species respectively. Signals were recorded at both of these m/z values, however their peak to baseline ratios are less than 1. While it can’t be definitively stated that H$_2$S is not present in the decomposition products, at best it is only present in trace amounts meaning that this mechanism is not a major decomposition pathway for this system.
Scheme 4-9: Proposed mechanism for the decomposition of metal xanthates by Chugaev elimination.

There is an alternative mechanism however whereby the xanthate could decompose via Chugaev elimination without the formation of $\text{H}_2\text{S}$. The first step proceeds as previously described, producing ethene in the process. In the next step the compound undergoes a second Chugaev elimination, this time involving both ligands. The hydrogen atom that was previously transferred onto the sulphur is transferred to another sulphur atom on the second ligand, freeing it. The first ligand decomposes further, releasing COS and leaving the metal sulphide. Depending upon whether the second ligand has already undergone Chugaev elimination of the alkene, the species released may either be a xanthic acid or dithiocarbonic acid. This mechanism is depicted in Scheme 4-9.

The presence of either or both of these two fragments would provide strong evidence for this mechanism occurring. Signals are indeed seen at the expected m/z values for both dithiocarbonic acid (m/z = 94) and xanthic acid (m/z = 124), however both of these signals can also arise from fragments that have previously been identified in literature, namely dimethyl sulphide and diethyl disulphide respectively.

While it is not feasible to pick out all the various fragments that would be associated with these byproducts to fully identify them, there is a structural difference between
the pairs of byproducts that may provide some indication as to which molecules are responsible for these signals. Both species produced by the second Chugaev mechanism contain -SH groups, while the ones seen in previous literature studies do not. Molecules with -SH groups would be be expected to have a reasonably high chance of becoming deprotonated when they are ionised due to the relative stability of the deprotonated ion. In contrast the dialkyl disulphides do not have labile protons, meaning that the ratio of the M-1 ion to the molecular ion is smaller. In both cases, no signal was detected at the M-1 value. This indicates that the acids are less likely to be present and the mechanism involving a second Chugaev reaction is likely not occurring.

In addition to the signals identified in Table 4.4 a number of other m/z values also exhibited peaks which coincided with the decomposition seen by TGA. In some cases these were common fragments, but others could not be explained by this. Some of the peaks could be explained by rational fragments of the starting compound, however without the full fragmentation pattern a positive identification could not be made.

The most compelling conclusion which can be drawn from study of these data is that the decomposition process for tin xanthate is not a simple mechanism and most likely is an amalgamation of a variety of competing processes, similar to the observation made by Chesman et al. in their study of cadmium ethyl xanthate.108

From the data it appears there are two possible routes by which the oxide could be forming during AACVD. The first is a continuation of the mechanism proposed by Vreugdenhil et al. wherein the deinsertion of CS₂ results in the metal alkoxide. Provided that the other xanthate has not undergone a similar deinsertion, a Chugaev elimination of S-ethyl-O-ethyl dithiocarbonate would result in the metal oxide as depicted in Scheme 4-10. In many ways this is very similar to the mechanism proposed by Chesman et al. describing the formation of COS, metal sulphide and S-ethyl-O-ethyl dithiocarbonate (see Scheme 1-7).

Another possibility is reaction of the formed metal sulphide with CO and CO₂. Such interactions have previously been seen with molecular metal-sulphur systems114 and more importantly with solid metal sulphides.115

\[
\text{EtO} + \text{M} \rightarrow \text{S} \quad \text{EtO} \quad \text{S} \quad \text{Et} \quad \text{S} \quad \text{EtO} \quad \rightarrow \quad \text{O=\text{M}} + \quad \text{EtS} \quad \text{S} \quad \text{EtO}
\]

Scheme 4-10: Possible mechanism for the formation of metal oxide through elimination of S-ethyl-O-ethyl dithiocarbonate.
With the elimination mechanism depicted in Scheme 4-10 it is difficult to see how the difference in conditions between the two types of experiment might lead to preferential selection of this decomposition pathway over the others discussed. The oxidation of the metal sulphide on the other hand has a much clearer precedent. TGA-MS clearly showed strong signals that could indicate the presence of elevated levels of both CO\(_2\) and CO during decomposition. Only a small amount of the precursor is present in the TGA-MS experiment however and so the source of the gases is quickly used up, causing them to drop back to background levels.

In the AACVD on the other hand the decomposition is a sustained process happening over the course of minutes to hours. During this time new precursor is constantly being introduced to the reaction chamber, decomposing and replenishing the CO\(_2\) and CO lost to the exhaust. Under these conditions the metal sulphide has much more opportunity to react with the gases forming the oxide instead. Holistically, this explanation seems more realistic as it does not rely upon a significantly different decomposition pathway dependent upon which conditions the precursor is subject to during decomposition. Rather, the identity of the resulting chalcogenide is dictated by the length of exposure to some of the gaseous decomposition products. The byproduct of this oxidation reaction is more COS, which has been shown by the TGA-MS experiment to already be present in significant quantities.

A depth profile XPS measurement of one of the films is plotted in Figure 4-11. The response from the XPS agrees with the results discussed in Section 4.3, showing a significant amount of oxygen present in the film.

There appears to be a periodic oscillation in the levels of oxygen and sulphur over the depth of the film such that as the level of oxygen rises, the level of sulphur falls and vice versa. The entire film was deposited over the course of 30 minutes, meaning that the period of these oscillations is roughly 10 minutes. The only aspect of the deposition process which would be expected to follow this oscillating pattern on this time scale is the temperature of the substrate. The temperature controller aims to keep the temperature of the substrate steady at the desired temperature during the course of the experiment, however some small variation of approximately 2 °C to 3 °C has been observed.

This observation lends further credence to the theory that reaction with CO\(_2\) and CO is cause of the metal oxide in the film. Fluctuation in the temperature would lead to variation in the equilibrium between the metal oxide and metal sulphide, with
the particular ratio at the time of deposition becoming “frozen in” as new material is deposited on top.

4.6 Inclusion of a secondary reductive sulphur source

As the precursor was not decomposing in the manner expected, a solution had to be found to counteract the formation of tin oxide during the deposition. The simplest solution to this would be to create a sulphur atmosphere within the reaction chamber. That way, the equilibrium between the metal oxide and metal sulphide is driven towards the metal sulphide. With a high enough concentration it should be possible to eliminate the oxide entirely.

Elemental sulphur is often used for the purpose of converting oxides to sulphides in a controlled manner, however in this case it is not suitable. This is because elemental sulphur is oxidising and the divalent tin is readily oxidised to tin(IV), resulting in SnS$_2$. Having said this, a study by Liu et al. details thermal annealing of SnO powders in a controlled sulphur-containing atmosphere which resulted in nanoparticles of SnS.$^{48}$ The levels of sulphur to which the SnO was exposed were regulated by the short annealing time (maximum 7.5 minutes) and the constant flow of argon over the system, preventing the concentration of sulphur in the atmosphere of the reactor from getting too high. While this approach might theoretically be feasible, it would require a second annealing step as it could not be performed at the same time as the deposition.

Hydrogen sulphide is an alternative sulphur source and has the added benefit of
being a reductive compound. With hydrogen sulphide the tin(II) will not be reduced any further, but any oxide present will undergo exchange to form sulphide. On top of this, any contaminant tin(IV) will be reduced to tin(II) in situ, hopefully resulting in a pure material. Hydrogen sulphide gas is unfortunately quite dangerous, being both poisonous and highly flammable. Significant precautions must be taken to ensure that it can be handled and used in a safe manner.

Thioacetamide (see Scheme 4-12) is a solid at room temperature, soluble in a number of solvents and can also act as a sulphur source: when heated above its decomposition temperature it breaks down into hydrogen sulphide and acetonitrile. The decomposition of thioacetamide proceeds via a two-step process, with the onset of the second step occurring at approximately $150^\circ$C.  

The active hypothesis was that with thioacetamide added to the precursor solution, no other alterations would need to be made to the reaction conditions: the thioacetamide would be carried by the aerosol into the reaction chamber where it would decompose to produce the required reductive sulphur atmosphere in a controllable manner.

Another film was deposited following the same procedure as previous films (see page 68). The only difference between this deposition and the previous one is that an equivalent amount of thioacetamide was dissolved into the precursor solution to give a 1:1 ratio of thioacetamide to Sn(S$_2$COEt)$_2$. The PXRD and Raman data collected from this film are displayed in Figure 4-13.

The arrow below the line in the PXRD picks out the (201) Si peak to which the pattern has been referenced. All other peaks in the spectrum match the peaks seen in calculated\cite{82} and experimental\cite{9,83} patterns for the recently identified $\pi$-SnS phase found in literature. The peaks have been assigned based on the calculated pattern provided by Abutbul et al.\cite{82} One significant peak is missing an assignment: this is because while the peak was present in the calculated pattern it had not been assigned.

Peaks in the Raman spectrum match reasonably well with those found in literature,\cite{9,83} although the peaks are subtly shifted to lower wavenumbers. Systematic shifts like these are often due to structural effects like crystallite size and stoichiometry. Where possible, peaks have been assigned their corresponding mode based upon the informa-

Scheme 4-12: Chemical structure of thioacetamide.
Figure 4-13: PXRD pattern (a) and Raman spectrum (b) of a film deposited from a 1:1 solution of Sn(S₂COEt)₂ and thioacetamide.

...tion provided by Abutbul et al., however as of the time of writing this information remains incomplete.

The peak at 262 cm⁻¹ is not identified in the reports by Ahmet et al. and Abutbul et al., however it is visible as a very small peak in the figures of both papers, and it is identified explicitly elsewhere. The peak at 202 cm⁻¹ is a barely visible shoulder on the 192 cm⁻¹ Aᵣ peak, which is consistent with previously reported data.

There is an extra peak of significant size at 310 cm⁻¹ which is not reported as a signal associated with π-SnS. The closest match out of the potential species present in the film is either Sn₂S₃ or SnS₂, which have signals at 307 cm⁻¹ and 312 cm⁻¹ respectively. Sn₂S₃ has a variety of other peaks in the region between 50 cm⁻¹ and 260 cm⁻¹, but there is no clear evidence of these in the Raman spectrum presented here. The peak at 312 cm⁻¹ in the spectrum of SnS₂ is known to be extremely intense, but the only other characteristic peak of SnS₂ is at 202 cm⁻¹ and of very low intensity, so may not be seen. In either case, there is no evidence in the PXRD pattern of the film that would suggest the presence of either of these materials.

EDXS data for the film is presented in Table 4.5. Measurements were taken from a variety of locations on the film and the results are very consistent. The ratio between sulphur and tin is very close to 1:1 with a slight deficiency of sulphur, which is a common property of SnS. Crucially, no oxygen whatsoever was identified in any of these measurements.

A study was conducted by Yago et al. in which the Sn/S ratio of α-SnS was varied...
Table 4.5: EDXS measurements of films deposited from a 1:1 solution of Sn(S₂COEt)₂ and thioacetamide. Si signal omitted for clarity.

<table>
<thead>
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</table>

between values of 0.88 and 1.28 in films deposited by thermal evaporation of elemental tin and sulphur at 800 °C with a substrate temperature of 300 °C. The findings were that the grain sizes of the films decreased with increasing Sn/S ratio above 0.93. A similar observation was made by Singh et al. Yago et al. also saw a variation in PCE of the resulting solar cells, peaking at a ratio of 0.91. They recorded no photovoltaic action above a ratio of 0.93 and hypothesised that this was due to short-circuiting of the cell by elemental tin.

Yago et al. used a very different method for deposition of the SnS film from the one studied in this chapter which resulted in a different phase of the material. Nevertheless, it highlights the potential importance of the stoichiometric ratio of the material on the film’s morphology, electronic properties, and ultimately its performance in a solar cell.

4.7 Film structure and morphology from 1:1 xanthate : thiocacetamide solution

To ensure that the substrate did not have an effect on the structure of the deposited material, glass and silicon substrates were placed side by side in the reactor and SnS films were deposited on them simultaneously. The films were tested by PXRD to make sure that resulting material was the same on the two different substrates. All peaks in the two patterns matched apart from the (201) silicon peak, which was missing in the pattern from the glass substrate as would be expected. A comparison of the two patterns can be found in Figure C-1.

Examining the films by eye, the film surface appeared to be very rough. Analysis
by SEM revealed that the film appears to be a network of needle-like crystallites. An example image is shown in Figure 4-14. Voids can clearly be seen between the crystallites which may account for the apparent roughness of the film. While the coverage of the surface is good, this morphology is not particularly suitable for inclusion in a solar cell due to the porosity. This is because any voids in the film act as a barrier to mobile charges and decrease the area through which carriers can move. In a material with a reasonably low conductivity this can be a serious issue. Additionally, if the voids are large enough they may allow other layers to permeate through them and come into contact with one another causing a short circuit. In order for the film to be suitable as a solar absorber layer the growth pattern of the film must be changed to obtain a more favourable morphology.

Attempts were made to modify the morphology of the film by modifying the parameters of deposition such as substrate temperature, flow rate and thioacetamide concentration, however these yielded no tangible difference in the morphology of the film.

4.8 Determination of film band gap

Optical measurements of the film were taken in order to determine the material’s band gap. The raw transmission and reflection data are presented in Figure 4-15. From the
transmission trace the absorption edge due to the material’s band gap is immediately visible, however there is a periodic oscillation in both the transmission and reflection data due to internal reflections in the film. This oscillation becomes apparent above 680 nm and so obfuscates the absorption onset caused by the band gap of the material.

As detailed in Section 2.6, the raw transmission and reflection data were processed to mitigate the effects of the internal reflections. The model which provided the most effective mitigation of these interference effects was a film with a single reflective interface. This model is described by Equation 4.1. The apparent lack of further internal reflections may be a result of the rough surface layer mentioned in the previous section. This would attenuate further reflections, leaving only the reflection off the interface between the film and the glass to contribute to interference.

\[ T \approx (1 - R)e^{-\alpha x} \]  

(4.1)

As mentioned in Section 4.1.2 the size and nature of the band gap of \( \pi \)-SnS is still under debate. Figure 4-16 shows the Tauc plots for indirect allowed and direct forbidden transitions based on the raw UV/vis data using the single reflective interface model to calculate \( \alpha \). Both of these plots exhibited linear regions which could be extrapolated to yield a transition energy. Plots for direct allowed and indirect forbidden transitions were also generated (see Figure C-2) but did not have a linear region, indicating that no such transitions occur within this energy window for this material.

Fitting the linear region of the traces gives an energy of 1.52 eV for the indirect
allowed transition and 1.62 eV for the direct forbidden transition. These values agree well with those found in literature (1.53 eV and 1.66 eV to 1.75 eV respectively), indicating that both types of transition are present in the material but that it is the indirect allowed transition which dominates the absorption profile of the material.

In summary, all of the techniques discussed here were in agreement that the film produced from a 1:1 solution of Sn(S₂COEt)₂ and thioacetamide was predominantly π-SnS. The Raman spectrum of the film did exhibit an extra peak that could not be assigned to any of the Raman active modes of π-SnS and most closely fitted the primary peak of the SnS₂ Raman spectrum, but no other measurements showed any sign of this material being present in the film. One possibility is that the laser used in the Raman measurement was causing damage to the film and changing its chemical structure, however no sign of damage was visible on the film through the confocal microscope after the measurement. Alternatively, the peak may be the effect of surface species, able to be picked up by the surface sensitive Raman technique but not by PXRD or EDXS.

4.9 Replacement of thioacetamide with thiourea

The results of the previous section indicate that while the addition of thioacetamide causes deposition of phase-pure π-SnS, the kinetics of the decomposition processes result in a film morphology which is not suitable for photovoltaic applications (this will be discussed further in Section 5.1.2). There are other compounds which can be used to
Scheme 4-17: Chemical structure of thiourea (a) with thioacetamide (b) for comparison.

provide a reductive sulphur atmosphere when heated above their decomposition temperature. Thiourea is a related compound to thioacetamide, with the only difference between them being the replacement of the methyl group with a second amine group (see Scheme 4-17). This change to the structure has a significant effect on the decomposition behaviour of the compound. For thiourea, decomposition begins at 187.5 °C with the evolution of CS₂, HNCS (isothiocyanic acid) and NH₃.¹¹⁸

Films were made following the same procedure as the one used for thioacetamide with the only difference being that thiourea was added to the precursor solution instead of the thioacetamide. Thiourea was found to be considerably less soluble in THF than thioacetamide, but eventually all of the solid dissolved into solution. It was immediately obvious from a cursory inspection of the films by eye that the new films did not have the same rough surface as those made with thioacetamide. Furthermore, there were no longer visible pinholes in the film.

Characterisation of the films was done in the same manner as with the thioacetamide-deposited films and a comparison of the results of PXRD and Raman are given in Figure 4-18. The pattern of peaks seen in the PXRD of the thiourea-deposited film is almost identical to that of the thioacetamide-deposited film, indicating that the material is the same and has the same phase. The peak widths appear to be unchanged by the change in sulphur source, indicating that this modification has not affected crystal strain or homogeneity. The main difference between the two patterns is the intensities of the peaks: some of the peaks appear to have greater intensity in the thiourea-deposited film, while others have a lesser intensity. This would indicate that the crystal growth kinetics of the various crystal faces is affected by the change in sulphur source.

The Raman comparison echoes these findings: the peak positions are very similar, although the relative intensities are different. Interestingly, the unassigned peak at 310 cm⁻¹ is still present, which may lend credence to the hypothesis that it is caused either by surface species or damage due to the laser.

Table 4.6 shows EDXS measurements collected from films made with thiourea as
Figure 4-18: PXRD (a) and Raman (b) comparison of films deposited using thioacetamide and thiourea as the secondary sulphur source.

<table>
<thead>
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<th>Sn</th>
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</thead>
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<tr>
<td>3</td>
<td>49.19</td>
<td>50.81</td>
</tr>
<tr>
<td>Mean</td>
<td>49.15</td>
<td>50.85</td>
</tr>
</tbody>
</table>

Table 4.6: EDXS measurements of films deposited from a 1:1 solution of Sn(S₂COEt)₂ and thiourea.
the secondary sulphur source. The stoichiometry is again very close to the desired 1:1 Sn:S ratio, and once again the material exhibits a slight sulphur deficiency. All of the measurements collected for the films deposited with thiourea have elemental ratios closer to unity than those deposited with thioacetamide, however the variance in the data is too large to draw statistical significance from this. A greater population of both types of films would need to be examined to obtain an accurate representation of this relationship.

As stated earlier, the morphology of the film is an important factor governing whether the film is suitable for use in a solar cell. SEM images of the film deposited from the solution containing thiourea indicated that the growth pattern in the presence of thiourea was very different. An example of this is shown in Figure 4-19. In this case the film does not appear to have any obvious voids. The crystallites are much more spherical and appear to be closely packed, with crystallite sizes of around 1µm.
Figure 4-19: SEM micrograph of a film deposited by AACVD from a 1:1 Sn(S$_2$COEt)$_2$ : thiourea solution.

4.10 Summary

In this chapter the compound tin(II) ethyl xanthate was studied and its potential as a precursor for SnS was assessed. Synthesis of the compound was found to be reasonably straightforward and could be performed both on the bench top and air-sensitively. That being said, a suitable method for purification of the product synthesised by the bench top method was not found and the product was found to contain significant levels of the by-product KCl. The compound was found to be temperature sensitive, meaning that refrigeration was necessary to store it for more than a few days.

As might be indicated by the temperature sensitivity the compound was found to decompose to SnS at a very low temperature. Unfortunately, films made using this precursor often had extremely low crystallinity, sometimes being completely amorphous. When crystalline material was produced it was predominantly SnO with small amounts of mixed sulphides. Investigation of the cause of this indicated reaction of the metal sulphide with decomposition by-products, leading ultimately to the oxide.

A secondary sulphur source was employed which rectified the issue of inclusion of oxygen in the films as well as eliminating higher oxidation state oxides. Interestingly, this also caused the resulting film to exclusively adopt the less common cubic phase $\pi$-SnS. A thorough investigation of the literature showed that the method developed
here constitutes the lowest temperature vapour-phase deposition of $\pi$-SnS to date. This is made even more significant by the fact that, as stated earlier, AACVD is a technique that is inherently scalable.

The phase pure films were characterised, but their suitability as a component layer in a thin film solar cell was in doubt due to their poor morphology. Tests were carried out to assess whether the films could be improved through tweaking of the deposition parameters, however none of the modifications attempted seemed to improve the film’s morphology at all. To avoid this problem an alternative sulphur source with a related structure but slightly different decomposition behaviour was tried. The outcome was almost identical when its analytical results were compared to the previous films, however in this case the visible pinholes were no longer present and the morphology of the film was significantly improved. These new films were deemed much more suitable for application in a solar cell and so the deposition parameters used here were transferred for use in the fabrication of a full device.

The ability to access the $\pi$-phase of SnS also gives a unique opportunity to investigate the interaction between SnS and group II metal sulphides when they are co-deposited. The work from this chapter is combined with the development of calcium sulphide precursors in the last chapter in an attempt to address this question.

References


Chapter 5

Tin sulphide thin film solar cells

5.1 Introduction

5.1.1 Thin film solar cells

While silicon makes up the vast majority of the current solar cell market, it is in many ways reaching the limit of its capability. More recently, thin film technologies (also known as second and third generation solar) have begun to emerge into the market. While the percentage of the total global market controlled by thin film technologies has not changed dramatically in the past two decades (in fact it has fallen from a high point of 17% in 2009 to just 5% in 2017), it has nonetheless still experienced significant growth due to the rapid expansion of the overall market.¹

One of the main attractions of many of the thin film solar technologies over the more established silicon is their improved material and energy cost with respect to manufacture. Silicon requires a very high energy process to extract and refine due to the high temperatures involved. Silicon solar cells also require significantly more material as silicon has an indirect band gap and a relatively low absorption coefficient in the visible and infra-red region of the spectrum.² This means that light has a longer path length through the material and so more material is required to make sure that as much energy as possible is absorbed. Improvements are still being made in this area however with improved efficiencies and better processing techniques and architectures allowing thinner wafers without sacrificing energy collection.¹

Thin films on the other hand tend to involve materials with much higher absorption coefficients, allowing excellent photon capture across the usable spectrum with as little as 300 nm of material. Of the wide variety of thin film technologies currently in development, only cadmium telluride (CdTe), amorphous silicon (a-Si) and copper indium
gallium selenide (CIGS) have reached the point of becoming commercially available.

5.1.2 Film morphology and cell architecture

The structure of thin film solar cells differs greatly from that of conventional silicon as charge separation is most commonly achieved by the electrical contact of different materials rather than selective doping of a single material (i.e. silicon). The structure of the device is generally a series of layers. Each layer has a specific purpose in the overall design to allow it to collect the incident light, generate electron-hole pairs and efficiently separate them to build up a potential difference across the device.

The fabrication of the device begins with a substrate. This material is often glass, but may also be a flexible polymer or other similar material. Usually the cell is designed to be illuminated through the substrate, hence the use of glass, but occasionally metal is used. Either way, one side of the cell must be transparent to allow light into the active layers. As an electrical contact is needed on both sides of the cell some sort of transparent conductor is used on at least one side of the cell. This role is usually filled by a transparent conducting oxide (TCO) such as indium-doped tin oxide (ITO), aluminium-doped zinc oxide (AZO) or fluorine-doped tin oxide (FTO). In these materials the natural metal oxide has a wide band gap and is classed as an insulator, but doping at a high enough density with a suitable heteroatom can provide enough free carriers to make the material electrically conductive while maintaining its optical transparency.

As discussed in Section 2.4 the beating heart of a solar cell is the p-n junction. In some forms of thin film solar cell two materials selected for their electronic properties, one p-type and one n-type, are deposited one on top of another to form the p-n junction. In some cases the p-n junction is also sandwiched between a pair of wide band gap materials termed “blocking layers.” Blocking layers are wide band-gap materials where one of the band edges sits close to the band edge of the contacted material, while the other is significantly different in energy from its counterpart. This allows the easy flow of one type of charge between the two proximate band edges while the other type of charge is blocked due to the large energy barrier required to move from the band edge of one material to the other. This concept is represented in Figure 5-1.

If chosen well, blocking layers are useful as they increase the efficiency of charge separation in the cell, which will increase the amount of energy which can be extracted from the cell. This comes at the cost of increasing the complexity of the cell however.
Blocking layers allow the construction of another form of photovoltaic device known as a p-i-n junction. Here a single absorbing semiconductor is sandwiched between one p-type and one n-type blocking layer. The “i” stands for intrinsic, as it is often an intrinsic semiconductor (i.e. a material which does not require doping to exhibit semiconducting properties) which is used in these devices. The interfaces with the blocking layers provides the charge separation required for the device to function.

The various layers involved are deposited one on top of another, masked or patterned in such a way as to be able to achieve electrical contact with both sides of the device without causing a short-circuit. Most commonly the cell will have a “monolithic” architecture with compact, planar layers stacked one on top of the other, each one ensuring that the two to either side of it are kept isolated from one another. One of the most common defects which can cause a cell to not work is the presence of “pinholes” in one or more layers of the cell, small holes in the layer which allow the two adjacent layers to touch. This subverts the charge separation process and provides a site for recombination, reducing the efficiency of the cell.

In some cases where materials have low conductivity or there is poor charge transfer between layers a different morphology called a bulk heterojunction is used. This is either done by depositing two poorly mixing materials at the same time (this is the basis for organic solar cells\(^3\)) or alternatively depositing one layer with a mesoporous microstructure, into which a second material can be infiltrated. This second method
was first used for dye-sensitised solar cells and was later incorporated and adopted into perovskite solar cells.

5.1.3 Tin sulphide thin film solar cells

One family of materials which has shown a great deal of promise as active layers for solar cells are the metal chalcogenides. This is with the exception of oxides as bonding with the electronegative oxygen atom tends to result in a wide band gap. A great deal of the combinations of metals and other chalcogenides however have smaller band gaps which put them in the region classified as semiconductors. CIGS and CdTe are examples of metal chalcogenides which have already been proven as viable solar materials, however the parameter space for metal chalcogenides is huge and many remain unexplored.

The only other thin film technology based on metal chalcogenides which has attracted significant attention thus far is copper zinc tin sulphide/selenide (CZTS). This is another quaternary compound with a kesterite (Cu$_2$(ZnFe)SnS$_4$) structure and is often deposited as a solid solution of Cu$_2$ZnSnS$_4$ and Cu$_2$ZnSnSe$_4$, varying the ratio to obtain the desired properties. The attraction of CZTS over the more proven chalcogenide technologies of CIGS and CdTe is it is made of relatively earth-abundant and non-toxic elements.

The drawback of systems such as these is their complexity - with so many different elements involved in the material it is easy for secondary phases such as binary and ternary metal chalcogenides to form. These secondary phases have a negative effect on the performance of the cell and are often difficult to identify.

It is not necessary to go to such complicated systems in order to find viable photoactive materials however. Computational modelling and theoretical calculation predict that many of the binary and ternary metal sulphides are also capable of high photovoltaic performance if the right supporting layers and cell structure can be found. As stated earlier, the potential of these materials remains largely untapped and a great deal more work is required to fully explore it.

Tin sulphide is one such material. The first mention of a solar cell based on tin sulphide appears in the work of Clemen et al. Their attempt was not successful however and it was not until 1994 that the first working tin sulphide solar cell was reported. The cell had a power conversion efficiency (PCE) of 0.29% and was based on a ITO/CdS/SnS/Ag structure. Interestingly, the authors had attempted to dope the tin sulphide with antimony sulphide to make an n-type SnS layer to form the p-n junction.
but report that this was not successful. Instead they used the known n-type material CdS, which became the most common n-type material for SnS solar cells.

While a number of studies on the deposition and morphology of SnS thin films were reported in the intervening years, it was not until 2006 that reports of complete SnS solar cells were again seen. Both new reported cells were based on the n-CdS/p-SnS junction, however the SnS layer was deposited in very different ways: electrodeposition leading to a cell efficiency of 0.81%\textsuperscript{11} and spray pyrolysis giving an efficiency of 1.3%.\textsuperscript{12}

In 2007 Gunasekaran and Iehimura demonstrated that cells using a Cd\textsubscript{1-x}Zn\textsubscript{x}S layer instead of CdS gave a greater photocurrent,\textsuperscript{13} however perhaps because of the increased complexity of the ternary material this was not widely adopted.

A year later, Ichimura and Takagi instead investigated replacing the CdS layer entirely with ZnO.\textsuperscript{14} Both orientations were tried, one with the architecture ITO/ZnO/SnS/In and the other ITO/SnS/ZnO/In. Unfortunately in the more favourable first configuration the ZnO layer partially dissolved during electrodeposition of the SnS layer, meaning that the cell showed no activity. The other configuration only achieved an efficiency of 0.01\%, which the authors attributed to the fact that the incident light was entering the cell and passing into the absorbing SnS layer first. This would mean that charge carriers would be generated far from the SnS/ZnO interface, meaning that most would undergo recombination before being able to reach the interface and be separated by the junction’s electric field.

The ZnO/SnS junction was again attempted in 2009 by Ghosh et al.\textsuperscript{15} This time the SnS layer was thermally evaporated, allowing the cell to be designed such that light would enter through the ZnO layer before being absorbed in the SnS layer near to the junction. However other issues marred the performance of the cell, resulting in an efficiency of 0.003\%.

Another report detailed the formation of a similar type of device deposited entirely by RF magnetron sputtering.\textsuperscript{16} Once again the basis for the window layer was ZnO, but in this case the material was doped with Mg to give a formula of Zn\textsubscript{1-x}Mg\textsubscript{x}O. This resulted in the architecture ITO/ZMO/SnS/Cu. The best performance was found when x = 0.2 and gave a PCE of 2.1\%. At the same time another report was published describing the use of Zn(OS)\textsubscript{2} as a buffer layer between the ZnO and SnS.\textsuperscript{17} This gave the architecture Mo/SnS/Zn(OS)/ZnO/ITO, which achieved a certified total-area efficiency of 2.04\%. This was improved still further by using congruent thermal evaporation of the SnS layer and doping of the Zn(OS) layer with nitrogen, achieving a PCE of 3.88\%.\textsuperscript{18}
Increasing the complexity of the cell still further, the current record efficiency for a solar cell based on an SnS absorber layer includes an extremely thin (<1 nm) SnO layer between the SnS and Zn(O S) layers.\textsuperscript{19} This resulted in cell efficiencies of 4.36\%.

Other metal sulphides have also been proposed as n-type counterparts to SnS. One such junction pairing is found in the report by Stavrinadis et al. wherein PbS is used as the n-type layer.\textsuperscript{20} In this study the SnS and PbS are synthesised as nanocrystals which are then dip-coated onto the substrate in layers. By modifying the size and interaction of the nanoparticles during synthesis and deposition the authors were able to achieve a cell efficiency of 0.5\%. Patel et al. instead employed In$_2$S$_3$, resulting in a cell efficiency of 0.55\%.\textsuperscript{21}

The first heterojunction based on TiO$_2$ and SnS was described by Wang et al. in 2010.\textsuperscript{22} In these cells a mesoporous TiO$_2$ layer was deposited, followed by infiltration of SnS through chemical bath deposition. This configuration yielded a power conversion efficiency (PCE) of 0.1\%.

This structure was significantly improved by the inclusion of a P3HT layer. Guo et al. deposited SnS onto mesoporous titania in the same way, only this time they deposited a layer of P3HT on top before deposition of the Ag contact.\textsuperscript{23} The cells produced in this manner set a new record efficiency for SnS-based devices at the time of 2.8\%.

SnO$_2$ has also been put forward as a potential material for pairing with SnS. The first example of a working cell involved electrodeposited layers of first SnO$_2$ and then SnS on an ITO-glass substrate.\textsuperscript{24} The cell was completed with an In metal back contact. While rectifying behaviour and photovoltaic activity were observed, the reproducibility of the cells was reported to be very poor and the maximum efficiency was estimated to be 0.1\%.

More luck was had with the tertiary metal oxide MgSnO. The amorphous MgSnO layer was deposited by a sol-gel method and then SnS was evaporated on top.\textsuperscript{25} The full architecture was FTO/MgSnO/SnS/Pt and exhibited an efficiency of 2.1\%.

While amorphous silicon is in itself a solar absorber material and controls a small fraction of the thin film solar market, it has also been paired with SnS to form a heterojunction. These attempt were not particularly successful however (PCE = 0.17\%\textsuperscript{26} - 0.42\%\textsuperscript{27}), especially considering that purely a-Si cells are capable of much higher efficiencies.

Organic materials have also been suggested as candidates for pairing with SnS.
Jain et al. formed a cell with a structure comprising ITO/PEDOT:PSS/SnS/Al (PEDOT:PSS is polyethylenedioxythiophene:polystyrenesulphonate) where the SnS layer was deposited by thermal evaporation. The grain size of the SnS was found to be of particular importance to the performance of the cells, and a maximum efficiency of 0.2% was achieved.

Far greater success was achieved with the pairing of SnS and P3HT (poly(3-hexylthiophene)) as active layers. This heterojunction structure was further improved by a mesoporous titania scaffold into which the SnS was infiltrated and a PEDOT:PSS layer on the other side of the P3HT, resulting in a structure comprising FTO/planar-TiO$_2$/meso-TiO$_2$/SnS/P3HT/PEDOT:PSS/Ag. This increased complexity paid off, affording a PCE of 3.0%.

The first SnS based homojunction was developed by Yue et al. in 2012. These cells were based on the growth of SnS nanowires by a CVD method. During the first part of the deposition process, B$_2$H$_6$ was introduced into the reaction chamber, causing p-doping of the SnS. Near to the end of the deposition PH$_3$ was introduced, this time n-doping the deposited material. This resulted in the nanowires being p-type at one end and n-type at the other. A contact material was deposited on top of the nanowires and completed cells made in this way had a PCE of 1.95%.

SnS has also found use in other solar technologies. Incorporation of SnS nanoparticles into either P3HT or MDMO-PPV (poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene]), for use in organic bulk heterojunction solar cells where the second organic material was PEDOT:PSS, demonstrated increased cell efficiency at high SnS loadings. The authors then took this a step further by chemically treating the nanoparticles, resulting in a layer of amorphous SnO surrounding the particles. This was found to increase the PCE by “an order of magnitude” to 0.1%.

Quantum dot sensitised solar cells (QDSSCs) using SnS nanoparticles as the sensitisier were demonstrated by Guo et al., achieving an efficiency of 1.03%. These cells employed a liquid electrolyte solution containing a redox couple (I$^-$/I$_3^-$, organic disulphide/thiolate or S$_2^-$/$S_x^{2-}$) and worked in much the same way as dye-sensitised solar cells.

SnS quantum dots have also been incorporated into the active layer of hybrid organic-inorganic perovskite solar cells. The quantum dots are reported to improve incident light absorption, carrier separation and carrier transport, resulting in a 25% improvement in efficiency of the cells to 16.8%.
An alternative use has been to employ SnS nanoparticles as the counter electrode in a dye-sensitised solar cell.\textsuperscript{35} The sensitisrer and electrolyte were the commonly used N719 dye and iodide/triiodide redox couple respectively. These cells performed comparably with those made using a Pt counter electrode, giving a PCE of 6.56%\textsuperscript{36}. This was later improved further to give 9.0% efficiency.\textsuperscript{36}

Owing to how recently the $\pi$ phase of SnS was correctly categorised and reliable methods of depositing it were developed, there are very few reports of $\pi$-SnS based thin film solar cells. Of those that do exist, most fall back on the CdS/SnS junction as the active structure.\textsuperscript{37-40} As such there exists very little precedent for the pairing of $\pi$-SnS with other materials for the formation of effective photovoltaic junctions.

In this chapter the procedure used to fabricate $\pi$-SnS films developed in Chapter 4 is employed to deposit layers of this material for use in a solar cell. Various materials previously investigated for use with $\alpha$-SnS are here screened for their suitability with this new phase.

## 5.2 Cell architecture

The architecture of the cells created in this work is as follows. The TEC-15 FTO glass substrate is cut to a square with sides of length 2.5 cm. A central section of the FTO layer is removed by the process described in Section 3.5.1. The subsequent layers are either deposited with the central section and parallel edges masked, or where this was not possible the layer in these areas was removed by mechanical or chemical etching. Finally, a mask was used in the deposition of the gold layer such that the cleared parallel edges were coated to obtain a good electrical contact to the FTO. In addition, six 6.25 mm$^2$ areas (referred to as “pixels”) were coated, defining the miniature solar devices which would be tested. An electrical path made of gold went from these 6.25 mm$^2$ back contacts to the cleared central section to provide an area for good electrical connection to the back of the cell. This description is represented in Figure 5-2.
5.3 Contact layer screening

As has been described previously, a single layer of an intrinsic semiconductor on its own sandwiched between two contacts is generally not enough to create a solar cell. This is because there is no driving mechanism to separate the generated electrons and holes. Without this separation an electric field is not able to be set up in the cell and so no electrical potential is generated between the two contacts.

To achieve the separation of charges, other layers are introduced to set up an artificial junction in the device. This can be done as described earlier by sandwiching the intrinsic semiconductor between a p-type and an n-type blocking layer, forming a p-i-n junction.

There are many known blocking layers for both p- and n-type contacts, but not all of them are suitable for all active semiconductor layers. Considering that the development of thin film solar devices based on $\pi$-SnS is still very much in its infancy, screening of potential blocking layers was required to determine a viable configuration.

A set of “incomplete” cells was created for this experiment, each containing the $\pi$-SnS and either a p-type or an n-type blocking layer sandwiched between the contacts. While a solar cell based on the p-i-n architecture would usually employ one of each type of blocking layer, a junction formed from just one of either kind of blocking layer along with the absorber material is enough to generate the required separation of charges such that a response can be measured. This simplification will come at the cost of efficiency however.

In these “incomplete” cells the blocking layer was deposited either before or after the $\pi$-SnS in order to account for the potential effects that the subsequent deposition processes might have on the previously deposited layers. The blocking layers tested were nickel oxide, mesoporous carbon, PEDOT:PSS, PCBM ($C_{70}$), titanium dioxide,
tin dioxide, mesoporous titanium dioxide and zirconium dioxide. Deposition parameters for each of these layers can be found in Chapter 3. Representations of the “incomplete” cells are shown in Figure 5-3.

Figure 5-4 shows the results of this set of experiments. For each configuration four cells were made, each with six pixels as described in Section 5.2. In some cases it was not possible to try the layer in configurations where the layer was both above and below the \( \pi \)-SnS layer. The mesoporous carbon layer could only be deposited after the \( \pi \)-SnS due to the fact that it is completely opaque. As the cell is built up onto a glass substrate through which light must pass, the opaque carbon would block the light from reaching the active layer.

Titania and nickel oxide were deposited in both configurations, however it was observed that the \( \pi \)-SnS rapidly lost its colour during the 500 °C deposition process when these layers were deposited on top of the \( \pi \)-SnS layer. This is most likely due to it being quickly converted to oxide in the ambient air. Predictably, Figure 5-4 shows next to no activity at all for these devices. As a result of this finding devices with the zirconia layer, mesoporous titania layer and zinc oxide layer deposited above the \( \pi \)-SnS layer were not attempted as these required similarly high temperatures. Similarly, Spiro-MeOTAD was not considered to be stable enough at the 200 °C required for SnS deposition for it to be deposited before the \( \pi \)-SnS.
While the \(\pi\)-SnS appeared to be inert to most of the conditions to which it was subjected (excluding high temperature), it reacted with the solution used for the chemical bath deposition of SnO\(_2\) and entirely lost its colour in the course of about two minutes. This was expected to be due to the tin(II) being oxidised to tin(IV) while the sulphur was substituted for oxygen. As a result, these cells showed no activity.

There is no doubt at all that the most effective layer was planar titania. It is interesting to note that while made of the same material, the mesoporous titania was significantly less effective. Mesoporous titania is usually employed to increase the surface area of the interface between the titania and the active layer to improve charge transfer. However, it is seldom employed alone and is usually deposited upon a substrate with a thin planar titania layer already present. This improves layer adhesion and charge transfer between the titania and the contact layer.

The only other potentially notable layers are PCBM and SnO\(_2\). Unfortunately however these are both hole blocking layers, as is the titania. Therefore, while the screening was able to identify a viable hole blocking layer, an electron blocking layer was not found.

Figure 5-4: Measured efficiencies of devices made with a single blocking layer of different materials paired with \(\pi\)-SnS in different configurations.
5.4 Monosulphide/disulphide cells

As mentioned in Chapter 4, SnS is an intrinsically p-type material. An alternative way to form a solar cell would therefore be to pair it with a suitable n-type material to form a p-n junction, rather than a p-i-n junction.

α-SnS cells have previously used CdS for this purpose, however this was avoided in this work due to the toxicity of cadmium. An alternative n-type material which was thought might match SnS was SnS$_2$. A well established AACVD deposition route for SnS$_2$ was already known (see Section 3.5) and it seemed that this might provide a route to a fully tin-based p-n junction deposited solely by AACVD. Furthermore it was theorised that due to the fact that both compounds had the same constituents, albeit in different ratios, this might provide a favourable interface for charge separation and transfer. This approach has been tried previously$^{41,42}$ but with limited success.$^{43,44}$

An SnS$_2$ layer deposited onto FTO glass by the technique described in Section 3.5 was analysed by PXRD. The pattern produced is presented in Figure 5-5. This pattern shows a number of sharp peaks, all of which can be assigned to either SnS$_2$ or the underlying FTO layer of the substrate.

It is immediately obvious from the results displayed in Figure 5-6 that the inclusion of the SnS$_2$ layer has had a negative effect on the devices. An explanation for this can be found in the work of Whittles et al.$^{45}$ In their paper on the band alignments of the various sulphides of tin they noted that while the idea of a SnS$_2$/SnS junction appears attractive on paper, the reality is that the conduction band edge of SnS$_2$ sits almost directly in the centre of the SnS band gap. This means that rather than forming a p-n junction and helping to separate generated charges the SnS$_2$ instead acts as a recombination centre for the charges generated in the SnS layer.
Figure 5-5: PXRD pattern of SnS$_2$ layer deposited by AACVD.

![PXRD pattern of SnS$_2$ layer deposited by AACVD.](image)

Figure 5-6: $V_{OC}$ a), $J_{SC}$ b), fill factor c) and efficiency d) statistics for cells made with an SnS$_2$ layer (structure: FTO/TiO$_2$/SnS$_2$/π-SnS/Au) as compared to those made without SnS$_2$ (structure: FTO/TiO$_2$/π-SnS/Au).

![Statistics for cells made with and without SnS$_2$.](image)
5.5 An electron blocking layer for SnS

Recent work by Ding et al. describes a $\alpha$-SnS solar cell using P3HT as an electron blocking layer, as well as a mesoporous-TiO$_2$ layer on top of the planar TiO$_2$ layer into which the SnS was infiltrated. With this architecture power conversion efficiencies of 3.0% were achieved.

An attempt was made to replicate this architecture using the $\pi$-SnS layer developed in this work. As explained earlier, it was thought that using a mesoporous titania layer as well as a planar titania blocking layer would increase the interface surface area between the active SnS and titania, improving charge transfer while maintaining good charge transfer through the planar layer.

P3HT, a known electron blocking material, had not been investigated up until this point, so its suitability for the $\pi$-SnS layer was unknown. The layers were deposited according to the procedures in Section 3.5.

Figure 5-7 compares the performance of the resulting cells to that of the cells using only planar titania as a blocking layer. Once again, the modifications to the cell resulted in a complete loss in efficiency. Interestingly however in this case it is predominantly the $V_{OC}$ which is lost while a good number of the devices have $J_{SC}$ values comparable with those found in the simple pl-TiO$_2$/$\pi$-SnS device. A measurable short-circuit current indicates that the device is at least generating charge carriers, however no power can be extracted from the device.

Some of the devices created in this experiment were carefully split through the middle of their active regions. The resulting sample was mounted vertically and imaged using FESEM to obtain a cross-sectional image of the layered structure. Figure 5-8 shows a representative cross-sectional image of one of the devices. The layered structure can clearly be seen, with the glass substrate at the bottom, a thin adhesion layer on top of it, the FTO layer in blue, mesoporous titania in cyan, $\pi$-SnS in red and P3HT in green. The planar titania layer cannot be seen with this technique due to the fact that it is only a few nanometres thick. The mechanical stresses put on the cell to fracture it have caused de-lamination of the mesoporous titania layer (or at least part of it) from the substrate, resulting in the void seen between the FTO and mesoporous titania layers.

The features of greatest interest in this image however are the $\pi$-SnS layer, the mesoporous titania layer and the interface between them. The $\pi$-SnS layer appears to be a compact solid layer. Splitting of the cell has revealed large flat areas of the material
Figure 5-7: $V_{OC}$ a), $J_{SC}$ b), fill factor c) and efficiency d) statistics for cells made with the structure FTO/plit-O$_2$/m-TiO$_2$/π-SnS/P3HT/Au as compared to those with structure FTO/plit-O$_2$/π-SnS/P3HT/Au.

Figure 5-8: Cross-sectional SEM of a device with pl-TiO$_2$/m-TiO$_2$/π-SnS/P3HT structure.
at what appear to be various angles, most likely to be grain boundaries along which the layer has broken. The mesoporous titania layer on the other hand is made up of many discrete nanoparticles, agglomerated together into a porous structure in which many tiny voids can be seen and giving a gravelly appearance.

For the cell to work effectively the $\pi$-SnS needs to infiltrate through the entirety of the mesoporous titania layer, maximising the interface through which charge transfer and separation can occur and ensuring efficient transport of charge. From the image it appears that the top third of the mesoporous layer has $\pi$-SnS successfully infiltrated into it: the material here appears compact like the $\pi$-SnS layer, but the granularity of the mesoporous structure can also be seen. Below this however the granularity becomes more pronounced and the voids become visible. This observation leads to the conclusion that the $\pi$-SnS layer has only partially infiltrated into the mesoporous layer and may account for the loss of performance in the devices.

While it is easy to imagine the mechanism by which the infiltration depth through a mesoporous layer by a precursor vapour might be limited, previous attempts to infiltrate mesoporous titania layers with materials deposited by AACVD have proved successful,\textsuperscript{46} even with thicknesses of the mesoporous layer up to 4 $\mu$m.\textsuperscript{47} This indicates that the infiltration of the films produced here are not beyond the scope of the deposition technique, but instead requires refinement of the deposition parameters to allow the precursor to reach the entire depth of the layer before decomposing.

To investigate this further mesoporous layers were deposited directly onto silicon and $\pi$-SnS layers were deposited onto them. Silicon was used in this experiment firstly because it provided a better, more conductive substrate for SEM and secondly it can be split with relatively little effort to give clean, straight edges.

The structure of the mesoporous layer can clearly be seen in Figure 5-9a, which depicts the cross section of an as-deposited layer of mesoporous titania on a silicon substrate. Figure 5-9b shows a sample of a mesoporous titania layer deposited in the same way with $\pi$-SnS deposited on top. In this image it is much clearer that the $\pi$-SnS has only infiltrated roughly a quarter of the way into the mesoporous layer, leaving the rest empty. This confirms the finding in the cross section of the full device.

Figure 5-9c shows the same sample at a lower magnification and highlights another previously unidentified feature. The same layers are visible, but on top of the compact $\pi$-SnS layer very large crystallites of $\pi$-SnS appear to have grown, creating an extremely uneven surface with large voids between the crystallites. The reason for this secondary
Figure 5-9: SEM images of as-deposited m-TiO$_2$ layer a), π-SnS on m-TiO$_2$ at the same magnification b) and at lower magnification c).
morphism is unknown as the deposition parameters were not changed throughout the deposition process and such structures had not been seen before.

Referring back to the cross-sectional image of the full device Figure 5-8, it appears that there may indeed be some of these crystallites present as evidenced by jagged protrusions from the surface of the gold layer. These protrusions appear much less tightly packed than in Figure 5-9c and smaller in size however. Whether deposition occurred differently in the full device or whether the deposition of further layers led to partial removal of the crystallites is unclear.

As such, the presence of these surface crystallites in the full device cannot be completely confirmed from these images alone. Further study would be required to determine whether the same phenomenon was definitely occurring during the deposition of the full devices, and that the protrusions seen were indeed these crystallites. Assuming that the observation is correct, this would provide another reason for the lack of performance in the devices containing the mesoporous titania layer. It would appear from Figure 5-8 that the crystallites are poking through the upper layers. This would mean that the P3HT blocking layer above is not complete and the $\pi$-SnS layer may be directly contacting the gold contact. This negates the purpose of the P3HT layer as the holes separated by the P3HT layer can simply recombine with the electrons at the interface between the gold and the $\pi$-SnS.

As only the top quarter to third of the mesoporous layer was infiltrated by the $\pi$-SnS, the simplest and least disruptive solution for this was thought to be creating a thinner mesoporous titania layer. To achieve this the same deposition parameters were used with the exception that less of the titania paste was used to make up the spin coating solution. Two solutions were tried, one using 24 mg titania paste to achieve a 2:35 paste:ethanol ratio ($5 \times$ dilution) and another with 48 mg paste for a 4:35 paste:ethanol ratio ($2.5 \times$ dilution). This was done because the titania paste contains stabilising agents and other compounds, the effects of which may not vary predictably when the paste is diluted differently. Furthermore, the deposition solution itself would be expected to have a different viscosity depending upon the amount of the paste used to make it.

The $\pi$-SnS layer was deposited on top of these substrates and the samples split and analysed by cross-sectional SEM as before. SEM cross-sectional images of these layers are displayed in Figure 5-10. In both cases it appears that the approach of creating a thinner mesoporous layer has had the desired effect of allowing the $\pi$-SnS to infiltrate all the way through to the substrate. This is indicated by the compact appearance of
Figure 5-10: SEM images of m-TiO$_2$ layers deposited from 2:35 a) and 4:35 b) paste:ethanol deposition solutions with π-SnS deposited on top.
the layer right down to the substrate and the absence of areas with the appearance of the unfilled mesoporous layer.

While the infiltration problem appears to have been solved, the other issue that became apparent in the previous set of samples, namely the large crystal growths on the top surface of the π-SnS film, is still present here. This is not surprising as the only change between this set of samples and the last one is the thickness of the mesoporous layer. A new set of cells using these thinner mesoporous titania layers were fabricated and tested but showed no activity, possibly because of the presence of the crystallites disrupting the subsequent layers.

5.6 Hybrid SnS-perovskite cells

Hybrid organic-inorganic perovskites have recently been of great interest due to their potential for extremely high efficiencies. They are also known to have a high tolerance for pairing with other layers. Using an established architecture, devices were fabricated incorporating the π-SnS layer instead of the NiO electron blocking layer, resulting in a device with layers FTO/π-SnS/MaPbI$_3$/PCBM/Ag.

Figure 5-11 shows the cell statistics for these cells. The performance of these cells is an order of magnitude greater than that of the best cells made using just the π-SnS, indicating that better efficiencies ought to be possible with this material. However this is far from an ideal system as perovskite cells routinely have efficiencies far greater than this. Efficiencies of perovskite cells made using the original architecture are regularly between 10 and 15%.

Once again there is interesting variation in the open circuit voltage and short circuit current measurements of the cells. This time, the majority of the cells have a fairly consistent $V_{OC}$. The $J_{SC}$ on the other hand is very variable and seems to be the main cause of the highly variable overall efficiency. Further research would be required to better understand why this is the case, however it is unlikely that π-SnS is a suitable material for this configuration of layers and the usefulness of a cell built in this way is questionable.
Figure 5-11: $V_{OC}$ a), $J_{SC}$ b), fill factor c) and efficiency d) statistics for cells made with the architecture FTO/$\pi$-SnS/MaPbI$_3$/PCBM/Ag.
5.7 Summary

This chapter describes attempts to take the material formed using the deposition method developed in Chapter 4 and incorporate it into the structure of a thin film solar cell as the photoactive layer. Due perhaps to the relatively recent identification of the $\pi$-phase and the lack of literature concerning it, little is known about its behaviour in a solar device and its compatibility with other materials used for this purpose.

Therefore, the initial focus of the work covered in this chapter was to screen various commonly used solar materials and attempt to find compatible pairings of layers from which a full device could be constructed. Of all the layers that were considered, only a handful produced an appreciable result, with titania producing by far the most effective pairing. None of the electron blocking layers in these trials showed any response at all, meaning that other materials would have to be sought to make up a complete device.

On reflection, this may not have been the most effective manner in which to conduct the screening as the efficiency of the cell would be limited by not having both an electron and a hole blocking layer to effectively separate charges. Thanks to the variability of the devices and lack of optimisation there is a possibility that the use of only a single blocking layer may have produced false negatives.

A potentially more effective but significantly more time consuming way to approach this screening would be to attempt combinations of both electron and hole blocking layers, however this would vastly increase the parameter space and there was not sufficient time to conduct a study of this complexity.

It is possible that the effectiveness of different layers when paired with $\pi$-SnS could be investigated in another way. The presence of an electric field set up between the two materials caused by the separation of charges could be probed using the Hall effect, whereby the deflection of the flow of electrons through a material by a magnetic field is measured. The internal electric field would be expected to perturb the expected electron flow, providing information about the layers’ compatibility. This technique was not available in the course of this work however.

It was hypothesised that the n-type material SnS$_2$ might be paired with the p-type $\pi$-SnS to form a p-n junction which might remove the need for blocking layers. This hypothesis was tested by depositing a layer of SnS$_2$ using a known procedure and then depositing the $\pi$-SnS directly on top. It was hoped that using layers made from different ratios of the same elements might result in a favourable interface, however the opposite was found to be true, the inclusion of the SnS$_2$ completely killed the efficiency
of the device. A possible reason for this was found in a computational study which suggested that the band alignment of these layers would result in a facile pathway for recombination.

A recent report showed that a Cd-free $\alpha$-SnS cell could be made using a mesoporous titania layer to improve charge transfer at the titania-SnS interface and P3HT as an electron blocking layer. Considering that titania had also shown promise when combined with $\pi$-SnS a similar architecture was tried using $\pi$-SnS as the active layer. The resultant cells generated almost no potential difference at all, which also meant that the efficiency of the cell was also essentially 0%.

Cross-sectional SEM highlighted that the $\pi$-SnS was not fully infiltrating into the mesoporous layer, most likely due to the pores of the material becoming blocked by deposited material before the precursor could make its way all the way through the layer. Crystallites with sizes of greater than 1$\mu$m were found to be forming on the surface of the $\pi$-SnS layer too which may have had a detrimental effect on the deposition of subsequent layers. The cause of these crystallites was not determined and further study would be required to discover their origin. Both of these observations point to a deposition process which requires optimisation for the particular form factor of the substrate on which the material is being deposited.

While the images strongly suggest that the use of a thinner mesoporous layer resulted in complete infiltration, this would ideally be backed up by more definitive evidence. A map of the location of the various elements present in the layers could be built up using EDXS mapping. This would give compositional information about every single layer in the device. If the layers were indeed fully infiltrated, signals from the sulphur and tin would be expected to be seen throughout the mesoporous layer.

$\pi$-SnS’s compatibility in a perovskite solar cell was also briefly investigated and while the efficiency of the cell was significantly better than anything achieved with $\pi$-SnS as the sole active layer, the cells performed much more poorly than equivalent cells using only MAPbI$_3$ as the active layer.

This chapter represents the very early stages of the development of a cell based on $\pi$-SnS and considerably more work would be required to realise a device with appreciable efficiency. While some progress was made towards finding layers which might be compatible with $\pi$-SnS, none of the experiments carried out in the course of this chapter yielded any appreciable conversion efficiencies. It is expected however that with more time to conduct a more thorough search of the parameter space a viable architecture
could be developed and the promising qualities of π-SnS could be properly explored.

References


Chapter 6

Xanthate-based calcium sulphide precursors for co-deposition with SnS

6.1 Introduction

As mentioned previously, the idea behind the work in this chapter was to investigate the interaction of tin sulphide and group II metal sulphides (namely calcium sulphide) when co-deposited to form a solid solution. Previous work has shown that such solid solutions do exist,\(^1\) the crystal structure and electronic properties dictated by the ratio of the two compounds to one another. This work aimed to replicate this finding by AACVD, with the aim of investigating the effectiveness of such materials in thin film solar cells.

Calcium sulphide is a highly ionic compound with a cubic structure. Pure CaS is a white solid, however its mineralogical form, Oldhamite, is a brown colour due to the inclusion of magnesium and iron in its composition. It is most commonly found in meteorites but has also been identified in connection with coal deposits.

6.1.1 Optical properties of calcium sulphide

The study of calcium sulphide has primarily been focused upon its optical applications. As a pure material calcium sulphide is not optically active, however when doped with other elements and compounds it has been shown to exhibit promising cathodoluminescence,\(^2,3\) electroluminescence,\(^4-9\) and photoluminescence,\(^2,8-17\) The dopants used to achieve this include silver,\(^8\) bismuth,\(^14\) cadmium,\(^6\) cerium,\(^17-19\) Cu(F),\(^2,8,9,12\) euro-
pium, lead, antimony, SiCl₄, samarium, terbium and TmF₃.

Initially, research was largely devoted to the development of thin-film electroluminescent devices (TFELs). These devices were developed for use in backlit screens and usually comprise a stack of thin films: a phosphor material sandwiched between two insulating layers, which in turn are contacted by a pair of thin film electrodes. One of these electrodes is a transparent conductor, allowing the light generated to escape. They operate by the application of an alternating current across the stack, setting up capacitive coupling between the electrodes and causing the phosphor to luminesce. The advantages of these devices are that they have a long lifetime, operate well over a wide temperature range, are relatively rugged and hard-wearing and have a wide viewing angle.

More recently electroluminescent displays have been rendered largely obsolete thanks to the rise and adoption of LED technology. LEDs have a number of advantages over TFELs: they do not depend on an alternating current and so can be used with the much more versatile direct current that power most electronic devices, they have a significantly shorter half-life and their cost of manufacture has fallen dramatically thanks to economies of scale.

This has provided a new niche for CaS however, making use of its phosphorescent properties to act as the phosphor in phosphor converted white LEDs. It has also been demonstrated to be capable of IR upconversion.

### 6.1.2 Deposition of calcium sulphide

CaS has most commonly been deposited as a thin film, however the formation and properties of CaS quantum dots have also been studied. The vast majority of processes used for deposition of CaS thin films have been batch processes, including atomic layer deposition (ALD), CVD, electron beam evaporation, magnetron sputtering and pulsed laser deposition (PLD). These processes are capable of producing high quality, uniform films with finely controlled properties, however they cannot be easily scaled up for industrial production and often require high energies and low pressures.

AACVD (discussed fully in Section 1.2) combines control over deposition of the material with the potential for industrial scalability. The deposition of CaS by AACVD has already been demonstrated by Kunze et al. In this study, the authors synthesised
and characterised a calcium thioacetate, $[\text{Ca}(\text{SOCMe})_2(15-\text{crown-5})]$, for use as a single source precursor for CaS. The precursor was found to decompose cleanly under inert atmosphere to form calcium sulphide as evidenced by PXRD.

Like metal thioacetates, metal xanthates also share this direct Ca-S bond, allowing them to act as single source precursors. In their 2017 paper Al-Shakban et al.\textsuperscript{36} describe a calcium methylxanthate compound and its potential as a single source precursor for AACVD however in their report deposition using this precursor and technique was not attempted. In this chapter, the suitability of the xanthate ligand for the synthesis of xanthate-based single source CaS precursors is investigated. A family of calcium ethyl xanthates has been synthesised and characterised and their performance under AACVD conditions assessed.

### 6.2 Synthetic methods

This section will discuss the methods used to synthesise Compounds 1 to 6. The compounds’ structures can be seen in Figure 6-1. The full synthetic procedures for these compounds are detailed in Section 3.6.

The first step in the syntheses was to form calcium ethoxide by direct reaction of calcium metal with ethanol under reflux. In this way ethanol acted as both one of the reactants and the solvent, forming a solution of the ethoxide which precipitates as a white solid when the solution cools. Using anhydrous ethanol for this reaction step results in the greatest possible yield for this reaction, but benchtop ethanol still provides very good yields (>90\%). Any water that is present in the ethanol reacts with the calcium metal to form insoluble CaO, which precipitates out and can be removed by filtration later in the synthesis.

At this point there are two further steps required to reach the final products: the $\text{CS}_2$ insertion reaction into the metal-oxygen bonds and the spectator ligand exchange. These steps can be performed in either order with comparable yields. In the case of Compound 1 the spectator ethanol ligands are already co-ordinated to the metal centre as a result of the previous reaction. $\text{CS}_2$ insertion can be performed directly in the ethanol solution. The product, Compound 1, is much more soluble in ethanol than the ethoxide and so as the reaction proceeds the white precipitate dissolves back into the solution, which turns yellow as the product is formed.

To prepare for ligand exchange for Compounds 2 to 6 the ethanol was pumped off in vacuo. The most effective way to perform the ligand exchange was to use toluene as
the solvent and add a small excess of the desired ligand to the mixture. This was then stirred overnight to allow for complete exchange.

In an early attempt to make the system with pyridine spectator ligands and its methylated derivatives (Compounds 3, 4 and 5), the desired ligand was used as a solvent. This method also successfully resulted in the ligand exchange, however isolating the product was difficult due to the excess ligand becoming entrenched and forming an extremely viscous, sticky liquid. The material was able to be redissolved in toluene, freeing the entrenched solvent and allowing isolation of a crystalline product. In comparison the synthetic methods detailed in section 3.6 are more economical both in time and amount of ligand required.

### 6.3 Crystal structures

The crystal structures of the calcium ethylxanthate compounds (Compounds 1 to 6) are shown in Figure 6-1. The single-crystal X-ray diffraction analysis confirms the insertion of CS$_2$ into both metal-oxygen bonds in all six compounds and shows that the resulting compounds are monomeric. Complete exchange of the spectator ligands is seen in all compounds.

Compounds 1, 2 and 4 exhibit a form of disorder in which some atoms have two possible locations in the unit cell. Where this occurs the two positions are depicted as faded ellipsoids and where applicable are given the suffixes ‘A’ and ‘B’. The crystal structures of Compounds 2, 5 and 6 include a molecule of toluene, indicating that the compound has co-crystallised with the solvent. The toluene molecules have been removed in Figure 6-1 for the purposes of clarity, however the full crystal structures can be found in Appendix A along with complete crystallographic information.

Almost all of the compounds adopt the same ligand configuration with the two xanthate ligands sitting on a plane with respect to one another. The exception to this is Compound 2, where one of the xanthate ligands is rotated by approximately 90° with respect to the other. This will be discussed further below, but first the geometry of the other five compounds will be studied.

Excluding Compound 2, the geometry of the compounds could be described as either trigonal bipyramidal or pentagonal bipyramidal, depending upon whether the xanthate ligand is acting as a monodentate ligand (i.e. the CS$_2$ group is acting as a single chelating site) or a bidentate ligand. Representations of these geometries are shown in Figure 6-2.
Figure 6-1: Crystal structures of calcium ethylxanthate complexes (Compounds 1 to 6). Hydrogen atoms removed for clarity. Thermal ellipsoids at 50% probability.
Table 6.1: Selected bond lengths for compounds 1 through 6 in Å.

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<tr>
<th>Compound</th>
<th>Bond Lengths</th>
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<tr>
<td>2</td>
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<tr>
<td>3</td>
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<td>4</td>
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<td>5</td>
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<tr>
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<td>1.341(3)</td>
</tr>
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<td>9</td>
<td>1.341(3)</td>
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</table>

*The atom is disordered. Bond lengths are for site A and B respectively.*

[X] = N, O

Pmdeta is a tridentate ligand and so the compound contains a single pmdeta ligand rather than three monodentate ligands. Co-ordinating nitrogens are labelled N31, N32 and N33 respectively.

N33 occupies an equatorial position due to physical constraints of the pmdeta ligand and so cannot be directly compared to the corresponding atom in the other compounds.

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Table 6.1: Selected bond lengths for compounds 1 through 6 in Å.
To determine which of these geometries best describes these systems, the interatomic distances and angles must be examined. Table 6.1 shows that within each xanthate molecule the carbon-sulphur bonds are very similar in length, not differing by more than 1.7\%\%. This suggests that the carbon atom sits roughly equidistant from the two sulphur atoms in the CS\(_2\) group. Furthermore, the table also shows that in all cases the calcium-sulphur bonds for a given xanthate ligand are within 6\% of each other, indicating that the CS\(_2\) group is co-ordinating in an isobidentate fashion.

With respect to bond angles, if the xanthates are co-ordinating as a monodentate ligand the X-Ca-C and C'-Ca-C'' angles (where X is the co-ordinating nitrogen or oxygen of the equatorial spectator ligand) should be 120\(^\circ\). Otherwise, if the xanthates are co-ordinating as bidentate ligands where each sulphur atom occupies a co-ordination site, the geometry is pentagonal bipyramidal and the carbon atom will be halfway between the radii of two co-ordination sites. Therefore the N-Ca-C angle will be $72 \times 1.5 = 108^\circ$, while the C'-Ca-C'' angle will be $72 \times 2 = 144^\circ$. From Table 6.2 it is clear to see that the angles observed resemble those expected for pentagonal bipyramidal geometry much more closely than trigonal bipyramidal.

Having reached this conclusion the arrangement of the ligands can now be rationalised. The CS\(_2\) group is a fairly rigid structure and its two co-ordinating atoms are close together as they are bonded to the same atom. Assuming moderately similar axial and equatorial bond lengths the xanthate ligand requires a relatively small angle between the two sites it occupies in order to minimise energy. As mentioned above, the ideal
X41-Ca-C11<sup>b</sup> 113.05  -<sup>e</sup>  107.84  109.78  109.97  108.51
X41-Ca-C21<sup>b</sup> 108.62  109.46/93.95<sup>a</sup>  108.75  99.07/112.17<sup>a</sup>  109.97  115.09
C11-Ca-C21  138.33  -<sup>e</sup>  143.40  150.89/137.96<sup>b</sup>  140.05  136.33
X31-Ca-X41<sup>b</sup>  88.46  71.14<sup>c</sup>  91.68  85.40  87.40  88.93
X41-Ca-X51<sup>b</sup>  88.13  70.21<sup>cd</sup>  92.69  89.68  87.40  83.88
X31-Ca-X51<sup>b</sup>  170.79  108.91<sup>cd</sup>  175.62  174.19  174.79  171.21

<sup>a</sup>The atom is disordered. Bond lengths are for site A and B respectively.
<sup>b</sup>X = N, O.
<sup>c</sup>Pmdeta is a tridentate ligand and so the compound contains a single pmdeta ligand rather than three monodentate ligands.
<sup>d</sup>N33 occupies an equatorial position due to physical constraints of the pmdeta ligand and so cannot be directly compared to the corresponding atom in the other compounds.
<sup>e</sup>C11 does not sit in the equatorial plane in this compound and so angle comparisons are meaningless.

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<td>174.19</td>
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</table>

Table 6.2: Selected interatomic angles for Compounds 1 through 6 in °.

equatorial-metal-equatorial angle is 72°, while the axial-metal-equatorial angle is 90°. This explains the apparent preference of the xanthate ligand to sit in the equatorial plane.

An interesting quirk that emerges from study of the bond lengths and angles is that Compound 5 has a plane of symmetry running through the middle of the complex. This is the reason why a number of the bond lengths and angles for this compound seen in Tables 6.1 and 6.2 are identical.

As stated earlier, Compound 2 cannot be analysed in the same way as the other compounds due to the arrangement of the ligands. This is the only compound with a tridentate spectator ligand. The co-ordinating nitrogen atoms of the pmdeta ligand are linked through a 2-carbon chain, meaning that they are further apart than the xanthate’s sulphur atoms and so can reach more distant co-ordination sites. Despite this they are still not far enough apart to easily reach between an axial and an equatorial site, exhibiting a N'-Ca-N” angle of approximately 70° for neighbouring co-ordinating groups on the chain. The pmdeta ligand adopts a κ³ co-ordination, forcing one of the xanthate ligands out of the equatorial plane. As a result there is significant distortion of the co-ordinating sphere and it is much more difficult to accurately ascribe a particular geometry to this complex.

Studying the compound, the best fit for the trigonal bipyramidal geometry is the orientation where C21 and N32 occupy the two axial positions, while for the pentagonal bipyramid the axial atoms are S11 and N31. By comparing the relative angles of the...
co-ordinated atoms to the ideal angles for a given geometry, a percentage difference can be calculated. The mean difference for a particular geometry gives an indication of how closely that geometry agrees with the observed geometry in the compound. Using this analysis for the two proposed geometries in Compound 2 the mean differences are 11.3% and 11.7%. As these values are so close to one another it is concluded that the true geometric description for this compound remains ambiguous and further study would be required to find a more definitive answer.

The Ca-X bond lengths (where X = N or O) show some notable trends. In all cases the axial Ca-X bonds are shorter than their equatorial counterparts. The nearest neighbour to the axial sites in any direction are at 90° when viewed from the calcium atom’s frame of reference. For the equatorial sites, the nearest neighbour is only separated by an angle of 72°. This causes more steric crowding around the equatorial sites, making it more difficult for the ligand to get so close to the central metal atom and so the equatorial bonds are longer.

Of the Ca-X bonds Compound 1 has the shortest bond lengths. The length of a bond is indicative of its strength and on the whole a shorter bond indicates that it is stronger. Oxygen is more electronegative than nitrogen, meaning that it will bind more strongly with the calcium atom. Therefore it stands to reason that, all else held equal, the Ca-O bond would be stronger and therefore shorter than Ca-N.

Compounds 3 through 6 are closely related in that all of them have spectator ligands based on pyridine. These compounds offer an opportunity to investigate the effects of functional group substitution on the ligand’s bonding strength. Both of the substituted groups are electron donating groups, the tertiary amine of the 4-dimethylaminopyridine (Compound 6) being strongly electron donating, while the methyl groups of the 3- and 4-methylpyridine (Compounds 4 and 5 respectively) are weakly electron donating. The extra electron density granted by the electron donating groups is felt around the ortho- and para- positions of the ring. Therefore in the cases of Compounds 5 and 6, where the substituted group is para- to the co-ordinating nitrogen, the electron density on the nitrogen would be expected to be increased. This would attract the metal centre more strongly resulting in a shorter, stronger bond.

Compound 4’s meta- substituted methyl group is in the wrong position to donate electron density to the co-ordinating nitrogen and so it has a negligible effect on the ligand’s co-ordination. From these observations the Ca-N bond lengths would be expected to follow the trend 6<5<4≈3. This trend is indeed seen in the axial ligands
but not in the equatorial ones, which instead follow the trend $6<4<5\approx 3$. The reason for this is presently unclear and may be a result of crystal packing effects. This would require further investigation to understand.

Compound 2 has longer Ca-X bonds than any of the pyridine derivatives. This can be explained by the nature of the orbitals in which the nitrogens' lone pairs sit. The nitrogen atoms in the pyridine derivatives are sp$^2$ hybridised, with two of the sp$^2$ orbitals and the lone p orbital involved in bonding with the ring. This leaves the lone pair in the remaining sp$^2$ orbital. In the pmdeta ligand the nitrogen atoms are sp$^3$ hybridised and so the lone pair sits in an sp$^3$ orbital. The reduced s-character of the lone pairs in the pmdeta makes it a poorer $\sigma$-donor, resulting in a longer, weaker bond.

While examining the trend in these bond lengths, it is worth attempting to put them into some sort of context against an expected bond length for the interaction of these atoms. There is no specific property for the interaction of a calcium ion with the lone pair on a nitrogen and arguably the parameter that most closely fits this type of interaction is the covalent radius of the atom. The covalent radii of calcium and nitrogen are 174 pm and 75 pm respectively, which results in an expected bond length of 2.49 Å. Comparing this to the values found in these compounds' crystal data Compounds 3, 5 and 6 are the only ones with at least one Ca-N bond that matches this value. Of these, only Compound 6 has an average Ca-N bond length that is comparable to the covalent bond length. All the other Ca-N bonds are longer than this. This finding suggests that the Ca-N bonds of these compounds are overall relatively weak.

Having established that the electron density and orbital structure around the chelating atom affects the Ca-X bond length, the broader effect on the compound is also of interest, particularly the interaction between the metal centre and the xanthate ligand. Overall, there are a number of weak trends seen in the structural data of these compounds which are revealed by taking a weighted average of the lengths of each type of bond. In this case, weighted average refers to the fact that while all values for bond lengths are included, in situations where an atom is disordered the contribution of the different bond lengths is scaled based upon the occupancy of each site. For example, if the atom has two potential sites with occupancies of $\frac{3}{4}$ and $\frac{1}{4}$ the contribution of each site towards the average would be scaled by these amounts. An average of the lengths of each bond type is used for comparison between compounds in order to reduce the effect of other factors on the length of a particular bond.

Plots of these weighted averages are included in Appendix A. A contraction in the
Ca-N bond length is seen across the family of compounds 2 to 6, as described above. This is associated with a slight lengthening of the Ca-S bonds, indicating that the increasing electron donation from the nitrogen atoms is reducing donation from the sulphur atoms. The change in length and associated change in strength of the Ca-X and Ca-S bonds is important when considering the decomposition mechanism of the compound. These trends indicate that small changes to the structure of the spectator ligands can potentially have an effect on the decomposition behaviour of the compound.

6.4 NMR spectroscopy

Full NMR characterisation of all six compounds is given in Section 3.6 and spectra are shown in Appendix B. Inspection of the NMR spectra does however give some indication of the effects of the different spectator ligands on the interaction between the metal centre and the xanthate ligands. All of the compounds exhibit a triplet at approximately 1.1 ppm and a quartet at approximately 4.6 ppm in their NMR spectra corresponding to the CH$_3$ and CH$_2$ groups of the xanthates’ ethyl chain respectively. As Compound 1 has ethanol as its spectator ligands a further triplet and quartet are present, as seen in Figure 6-3. There is a marked difference between the signals from the two ligands: the more downshifted triplet and quartet, corresponding to the xanthate ethyl group, are much sharper and more clearly defined than those of the ethanol ligand.

The integral ratio of the sharp xanthate signals to the more broad ethanol ones is 2:3, agreeing with the ratio of two xanthate ligands to three ethanol ligands seen in the crystal structure. Furthermore, the relationship of the peaks can be confirmed by analysis of the coupling constants. The sharp peaks both exhibit a coupling constant of $J = 7.2$ Hz while the broad peaks both have a value of $J = 6.7$ Hz to 6.8 Hz.

The width of the peaks indicates that the ethanol ligands are fluxional at room temperature, switching between the subtly different axial and equatorial positions, while the xanthate ligands remain fixed in their positions.

A comparison of the triplets and quartets corresponding to the xanthate ligand’s ethyl group is displayed in Figure 6-4. With the exception of Compound 1 the multiplet positions show a clear trend, shifting further downfield (increasing ppm) going from Compound 2 through to Compound 6. This shift indicates an increase in acidity of the associated protons.

Having established in the previous section that the electronic structure of the spec-
Figure 6-3: $^1$H NMR spectrum of Compound 1 showing ethyl triplets and quartets.

Figure 6-4: Comparison of $^1$H NMR multiplets in Compounds 1 to 6.
tator ligands can affect the bonding of the xanthate ligand to the metal, the trend seen in the NMR shift may also be linked to the same effect. It is important to note however that SC-XRD and NMR analyse the material in two different forms: one as a solid and one in solution. As such only tentative correlations can be drawn.

To determine whether the two observations could be linked, the intervening bonds can be analysed in the same way as the Ca-X and Ca-S bonds. The results of this analysis can also be found in Appendix A.

In brief, as the Ca-N bonds contract the C-S bonds of the CS$_2$ group lengthen. The positively charged metal centre helps to stabilise the delocalised negative charge on the CS$_2$ group, so as this stabilising influence retreats the group is destabilised and the bonds lengthen accordingly. This causes the bond between the carbon of the CS$_2$ group and the adjacent oxygen to shorten, which in turn causes the methylene carbon-oxygen bond to lengthen.

The proximity of the electronegative oxygen atom would be expected to draw electron density away from the hydrogen atoms. Therefore, as the C-O bond lengthens the effect of the oxygen atom would be expected to diminish, resulting in greater electron density around the hydrogen atoms and shifting their associated multiplets upfield (lower ppm).

The data collected by NMR shows the exact opposite trend. It is not immediately apparent what the reason for this effect might be and further study would be required to understand this phenomenon. The $^{13}$C NMR (included in Appendix B) was also analysed but no trend was visible in the data.

### 6.5 Decomposition of solid precursor

To investigate the decomposition products of this molecular system a sample of Compound 1 was loaded into an annealing tube which was evacuated and refilled with argon three times to remove residual atmospheric gases. The tube was then placed in a furnace at $400\,^\circ\text{C}$ for one hour to allow for full decomposition of the precursor. Once this was complete the tube was allowed to cool to room temperature with the residual compound (a white solid) under the inert atmosphere. The solid was then broken up using a glass rod and the resulting powder was immobilised on a glass slide using a small amount of silicone grease. This sample was analysed by PXRD, the results of which are shown in Figure 6-5. The red lines indicate the pattern expected for bulk CaS (oldhamite) as detailed in JCPDS PDF #75-0261. All of the peaks seen in the pattern recorded here
match with those in the pattern and the peak intensities are reasonably close to those expected for the bulk material. This indicates that the precursor can indeed form CaS through decomposition.

The most obvious feature of the collected pattern is the broadness of the peaks. As has been stated in the previous chapter there are many causes for the broadening of peaks in the PXRD pattern, but in this case the most likely explanation is the size of the crystallites. Specifically, the broadness of the peaks suggests that the crystallites are very small. This is most likely a result of the manner in which the compound has decomposed.

The conditions under which this decomposition occurred favours nucleation of a very large number of small crystallites. This means that none of the crystallites are able to grow very much before they come into contact with other crystal domains. For a relatively ionic, binary compound such as CaS long intervals at high temperatures would be required for crystal domains to rearrange themselves and allow the crystallites to grow further and absorb one another (a process known as Ostwald ripening\textsuperscript{37}). The length of the annealing step used in this experiment is not long enough for this process to happen to a measurable degree and so the crystallites remain very small.
6.6 Decomposition analysis

The decomposition profiles of the compounds were investigated by TGA. The full traces from each compound are shown in Figure 6-6. The traces have some similarities in form, each showing a major decomposition step between 50 °C and 200 °C and another minor step at around 330 °C. This profile matches the one observed by Bezougli et al.\(^\text{38}\) in their study of calcium xanthates. Very similar profiles have also been seen with other metal xanthates including nickel,\(^\text{39}\) zinc,\(^\text{40,41}\) cadmium\(^\text{42}\) and iron.\(^\text{43}\)

The measurements displayed in Figure 6-6 show that the high temperature step is much the same between different compounds, while the low temperature step varies with ligand identity. This may help in determination of the decomposition pathway(s) of these calcium xanthates.

The majority of the compounds have onset temperatures for the initial decomposition step clustered between 50 °C and 125 °C. There is no clear trend in the onset temperatures and as such no direct links can be made between the observations of the compounds’ structures made earlier and their behaviour during decomposition. No pattern could be drawn between the physical or chemical properties of the ligands and the decomposition of their associated compounds either.

The fact that the compounds exhibit different onset temperatures for decomposition indicates that the decomposition is linked in some way to the identity of the ligands involved. It appears however that the connection is a result of a complex interplay of factors that cannot be distilled from this work.

The ligand in Compound 2 (pmdeta) is unique among the ligands used in this study
as it is the only polydentate ligand. As such it is significantly more difficult to remove the ligand from the metal centre and doing so will require a higher temperature. Table 6.3 shows that the onset temperature of Compound 2 is significantly higher than that of the other ligands. This may suggest that the rate of the initial decomposition is dependent upon the removal of the spectator ligands. This hypothesis will be investigated further later on.

Table 6.4 shows the residual masses of the compound samples after TGA. In all cases, the residual mass is significantly higher than what would be expected for CaS. For most of the compounds the difference between the expected and observed mass is around 4.2%. The exceptions are Compound 3 (2.5%) and Compound 6 (4.6%). This suggests that the product of the decomposition of these compounds under these conditions is not pure CaS and contains impurities.

Considering the temperatures involved, some form of organic impurity is unlikely

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<th>Minor step</th>
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Table 6.3: Onset and endpoint values for Compounds 1 through 6 (in °C).

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<tr>
<th>Compound</th>
<th>CaS expected</th>
<th>CaCO₃ expected</th>
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<td>1 (EtOH)</td>
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</tr>
<tr>
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</tr>
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</tr>
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<td>4 (3mpy)</td>
<td>12.8</td>
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<td>5 (4mpy)</td>
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<td>17.0</td>
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<td>6 (4dmap)</td>
<td>11.1</td>
<td>15.7</td>
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Table 6.4: Residual masses for Compounds 1 to 6 measured after TGA.
as these would be expected to have decomposed by this point. As the residue was a
white solid, elemental carbon can also be ruled out. One possibility would be CaCO$_3$;
the potential for metal xanthates to break down to oxides and also generate CO$_2$ has
already been demonstrated in Chapter 4 and in the presence of CO$_2$ calcium oxide is
known to spontaneously form CaCO$_3$.

The expected residual masses for CaCO$_3$ have also been included in Table 6.4,
however almost all of the residual masses are lower than this. The exception here is
Compound 6, whose residual mass is 0.3% greater than what would be expected for
CaCO$_3$. This could be a sign that there is another even heavier compound present
in the residual material, however the difference here is too small to draw a definitive
conclusion and could simply be due to experimental error.

Combining these observations with the findings from decomposition of the solid
precursor, the most likely explanation these observations is that there is some CaS
present in the decomposition products (as evidenced by PXRD), but this is mixed with
an unknown fraction of one or more heavier compounds.

TGA-MS analysis of the compounds was also performed. The plots generated from
these experiments are presented in Figures C-4 to C-9. In all cases there are clear signals
at various m/z values associated with the mass loss events seen in the TGA. Crucially,
some of these signals are not seen during all decomposition events. By analysing which
signals are specific to certain steps, information about the mechanism involved in specific
steps can be deduced.

The first signal of interest is that at m/z = 34. There are only three obvious sources
for a signal at this m/z value: $^{34}$S, H$_2$S or a doubly ionised fragment of mass 68 Da.
While elemental sulphur is expected to be present as a result of the fragmentation of
volatile sulphur containing species and approximately 5% of this would be $^{34}$S due to
natural abundances, the shape of the signal tells a different story.

Unlike the signal for m/z = 32 ($^{32}$S), there is no peak for m/z = 34 associated
with the second decomposition step seen in the TGA. This would suggest that the
fragment responsible for this signal is only being produced in the first decomposition
step and is independent of the fragment or fragments giving rise to the m/z = 32
signal. The signal at m/z = 68 also shows peaks during both decomposition steps,
suggesting that doubly ionised species are also not the cause. Having eliminated these
other possibilities this would suggest that the most likely candidate for this signal is
indeed H$_2$S, however there is no evidence of C$_2$H$_4$ whose strongest signal is expected
at m/z = 27 for the fragment with one missing hydrogen atom. As a result it seems unlikely that the Chugaev elimination mechanism proposed by Alam et al. is occurring in the decomposition of these precursors. Having established this it is not entirely clear what the source of the H₂S is.

Another set of important signals in these decompositions are those at m/z = 60 and 76 (and the related isotopic signals m/z = 61, 62 and m/z = 77, 78 respectively). As was seen in Chapter 4, these signals are in agreement with the proposed mechanisms by Vreugdenhil et al. whereby COS and CS₂ (along with CO₂) are major components of the decomposition byproducts.

Of greater interest however is the fact that all of these signals again only occur during the initial major decomposition step. This holds true for all six of the compounds. Furthermore, signals at m/z = 79 (corresponding to the strongest signal in the pyridine mass spectrum) are seen for compounds 3 to 6, signals at m/z = 93 (methylpyridine) are seen for compounds 4 and 5 and signals at m/z = 121, 122 and 123 (4-dimethylaminopyridine) are seen for compound 6. All of these signals are also only seen to occur during the first decomposition step.

Conclusive evidence of whether CO₂ was being produced could not be determined in these experiments. Normally, by calculating the ratio of the peak current to that of the baseline on such a signal, the background effect of the increase in pressure can be estimated. This can then be compared to the ratios of other peaks with their baselines to indicate whether the peak is likely to be due to the release of a fragment of that m/z value, or just the effect of the pressure change as stated previously.

There are two reasons why this approach cannot be used here. Firstly, calcium has a mass of approximately 40.1 Da and while it is extremely unlikely that isolated calcium ions would be generated in the exhaust gas or mass spectrometer, this cannot be completely ruled out. Secondly, a satisfactory baseline could not be fitted to these signals, so a reliable ratio could not be extracted. Having said all this, based on the observations made in Chapter 4 and in literature the evolution of CO₂ is very much expected here too.

All of this information suggests that the major decomposition step involves rearrangement of the xanthate molecule, deinsertion of the heterocumulene and loss of the spectator ligands around the metal centre. This would result in a mixture of metal alkoxides and metal thioalkanes, which could explain why the residual mass after the first step cannot be attributed to any single intermediate of the precursor.
In all six compounds the m/z signal peaks corresponding to the heterocumulenes begin and reach a maximum earlier than those corresponding to the various spectator ligands. This suggests that the decomposition of the xanthates begins before the loss of the other ligands. Therefore, the differences in decomposition onset cannot be attributed to the loss of the ligands being the initial step. Instead, the presence of the ligands must have an effect on the electron distribution in the xanthate molecule which in turn affects its stability.

No consistent m/z signals could be found which only appeared during the second decomposition step of the reactions, making it much more difficult to identify key species in this second step. The signal at m/z = 72 appears only during the second step for all compounds except Compound 1, where it appears in both. This signal could correspond to C$_4$H$_8$O (an unsaturated diethyl ether) and so could be the result of Ca(OEt)$_2$ breaking down to form CaO and Et$_2$O. This is analogous to the thermal decomposition of Ca(OH$_2$) to form CaO and H$_2$O, which occurs at similar temperatures. There is not enough evidence however to verify this hypothesis.

Considering that ethanol is the spectator ligand in Compound 1, it would not be too much of a stretch to imagine that reaction of volatilised ethanol molecules with other decomposition byproducts might result in the formation of this compound and explain the presence of the extra peak.

While this analysis does offer some interesting insights into the decomposition pathways these materials exhibit, further research is required to fully make sense of the observations.

### 6.7 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry of a precursor can reveal a lot of information about the thermal behaviour of the compound, including the manner in which it decomposes. In TGA the signal only changes when the mass of the sample changes: i.e. when some of the mass of the sample is lost as volatile byproducts. In contrast DSC tracks the observed heat capacity of the sample meaning that as well as reactions involving the loss of molecular fragments, phase transitions and reactions which do not involve mass loss are also detected. Combining the two can give a much greater understanding of the manner in which the compound behaves as it decomposes.

Figure 6-7 shows the DSC and the first derivative of the TGA traces for each of the six compounds. The first derivative is used here as the mass loss events are represented
Figure 6-7: Combined DSC and 1st derivative TGA plots for Compounds 1 through 6.
by peaks which can more easily be compared with the peaks seen in the DSC trace.

A feature that all of the DSC traces share is at least one sharp peak between approximately 70°C and 150°C. Sharp peaks are most commonly indicative of phase transitions, however they can also be the result of chemical reactions. In general a first order reaction such as an intramolecular reaction would be expected to exhibit a sharp peak as it is not dependent upon the proximity of multiple species. In contrast, second order reactions tend to be broad, as the reaction cannot happen until the species involved collide. Considering the results from the TGA-MS analysis, this peak may well be the signal from the deinsertion reactions, although in Compound 2 the primary sharp peak occurs very late in the decomposition step.

The general shape of both traces for each compound are surprisingly different. This indicates that the identity of the other ligands has a strong influence on the decomposition of the compound. The major decomposition steps of all of the compounds are accompanied by a multiple overlapping peaks of various shapes and intensities, indicating a multitude of processes involved in each step. As such, enthalpies of reaction cannot be reliably extracted from these data.

The second decomposition step can be seen as a small bump in the first derivative of the TGA, but interestingly there are no obvious signals in the DSC traces that can be linked to this decomposition step. One possibility is that the enthalpy of reaction for this step may be very small, although no data on this could be found. Alternatively this could be a result of the difference in conditions under which the two experiments take place. TGA requires an open sample pan to allow the gases produced during decomposition to escape so that the difference in mass can be measured. In DSC the sample pan must be sealed as any change in the amount of sample present would skew the results and make the measurements meaningless.

The signal in the TGA indicates that there is some mass loss during this event, indicating that gases would be produced. The gases produced during the first decomposition step would still be present in the DSC pan, meaning that it would be under significantly higher pressure than the sample in the TGA. This may hinder the progress of the later decomposition step as the production of more gases is less favoured.

6.8 AACVD of CaS precursors

The general procedure used for AACVD of Compounds 1 to 6 is detailed in Section 3.6.7. Full details of the AACVD experiments carried out with these precursors is detailed in
Table C.1, however the experiments of particular importance will be described here.

Analysis of the TGA data collected for these compounds suggested that full decomposition of the precursor to the metal sulphide was not achieved until the second decomposition was complete. The endpoint of this second step was usually around 380°C to 400°C. Using this information an experiment was run with a reactor temperature of 400°C. Toluene was used as the solvent and the gas pressure was set to 20 psi, giving a flow rate of 1.5 L min⁻¹.

After the deposition the substrate was removed and examined. No deposition appeared to have occurred on the heated part of the substrate whatsoever. The ends of the substrate that extended beyond the length of the furnace were covered in a powdery white film however. Inspection of the reactor tube revealed the same phenomenon - the ends of the tube both “before” the furnace and “after” it had the same white powdery film, but there was nothing deposited in the area which was within the furnace.

The best explanation for the observations made in this experiment is that the reactor temperature was too hot. The precursor appeared to be breaking down in the vapour phase before reaching the substrate, forming solid particulates that would not then interact further with the substrate or one another, hence the white powder. This is described by Process 4 as detailed in Section 1.2.2, whereby the solvent and precursor are vaporised before reaching the substrate, the precursor then breaks down while still in the vapour phase. The product, unable to maintain the vapour phase, precipitates as a fine powder. The curious lack of any powder on the heated part of the reactor and substrate could be explained by convection currents set up near the heated surfaces - these would keep the fine particulates airborne as they travel over the heated surfaces. The film deposited on the unheated section of substrate was analysed by PXRD, but no signals were seen. This is likely due to the low density of the sample and expected extremely small crystallite size.

In light of these results, further experiments were tried at temperatures of 350°C, 300°C, 200°C, 150°C and 120°C but the results of these experiments echoed those of the first. It was observed in each case though that the “front” of deposited material moved closer to the heated area of the furnace as the temperature was lowered.

At temperatures of 110°C and below a poorly adhered white powdery film was produced across the entire substrate. The boiling point of toluene is 110°C so at these temperatures it was no longer a viable carrier solvent. THF and ethanol were used as alternatives.
Figure 6-8: An example of a film deposited from Compound 1 at 100 °C with ethanol carrier solvent. The film shows four distinct regions: before the furnace a), furnace front (not directly heated) b), furnace centre (heated) c), and furnace rear (not directly heated) d).

Figure 6-8 shows an example of a film deposited at 100 °C using a precursor solution of Compound 1 in ethanol. 100 °C was found to be the optimum temperature to achieve the most consistent film across the substrate. Despite this, the film clearly shows four distinct areas as labelled. The first area was before the furnace and so was not heated. It is likely that some heat was transferred here from within the furnace, but it is expected that this region was significantly below the onset point for decomposition.

The second and fourth areas, labelled b) and d) respectively, were within the furnace but were not directly above the heating element. As such, they were heated but the temperature would not reach 100 °C. The majority of the product material settled in these regions, giving a thicker covering. The area marked c) was in the centre of the furnace, located next to the heating element and thermocouple. While there is some deposition here, the coating is thinner than in the other areas, mirroring what was seen in previous experiments.

To test that the change of solvent wasn’t the reason for the formation of the film further experiments were run using THF and ethanol with higher deposition temperatures. These experiments had the same results as those performed with toluene however.

The parameters of the deposition process were varied in an attempt to improve the morphology of the films produced at 110 °C and below. These variations included the gas pressure (10 psi to 30 psi giving a flow rate of 1.0 L min⁻¹ to 2.25 L min⁻¹) and

Figure 6-9: An example of a film deposited from Compound 4 at 100 °C with THF carrier solvent.
solution concentration (50 mM to 150 mM). Using THF as the carrier solvent was found to improve the uniformity of the film as can be seen in Figure 6-9, however none of the process modifications had any effect on the film morphology.

The poor adhesion of the film is demonstrated in Figure 6-9: a silicon substrate is located at the end of the glass substrate to catch some of the settling material. Where it has moved during removal from the reactor, it has significantly disturbed the material on the glass.

6.9 Analysis of deposited films

Having established a process by which a film could be produced using these xanthate-based precursors, an attempt was made to analyse the resulting films. This section details the analysis of some films made with this process using Compounds 1, 2 and 4. Full investigation of the other compounds was not completed.

Figure 6-10 compares the PXRD patterns of a film before and after annealing with the pattern of the precursor (Compound 2) used to make it. No background subtraction was performed on these patterns as the peak intensities are very low. The first thing to note is that the pattern of peaks seen in the precursor compound disappear entirely in the films. This indicates that the material has at least partially decomposed. As would be expected from a new compound, the pattern obtained from the precursor does not match any patterns in the database. Analysis and assignment of the peaks in this pattern is beyond the scope of this work.

No peaks at all are seen in the pattern of the freshly deposited film. The only feature of this pattern is the hump in the background of the pattern from the glass substrate. This indicates that the film is either amorphous, or there is not enough of it to get a signal.

The extremely low deposition temperatures required in order to deposit material on the substrate were known to not be sufficient for complete decomposition of the precursor, as evidenced by the TGA traces discussed earlier. In fact, the decomposition was not completed until the TGA furnace reached 380 °C. To address this the film was annealed in an inert atmosphere at 400 °C for 1 hour to complete the decomposition process.

The pattern for the annealed film is almost identical, save for a small peak at $2\theta = 29.6^\circ$. This peak does not match the pattern for CaS, however there are multiple patterns with a peak at this $2\theta$ value. One of these patterns is CaSO$_4$, however in this
Figure 6-10: PXRD pattern of Compound 2, a film deposited by AACVD using Compound 2 and the same film after annealing in an argon atmosphere.

In the case the much more likely cause is either CaO or CaCO$_3$. Of the two of these, the peak most closely matches CaCO$_3$, however as there is only one peak a positive identification cannot be made just from this pattern.

The peak in this spectrum is of extremely low intensity which would indicate that either the material is not very crystalline or there is not a lot of material present to diffract the X-ray beam. Potentially the cause could be a combination of both of these. The peak is also quite broad, most likely due to material heterogeneity and/or crystallite size.

Figure 6-11 is an image collected of the film by SEM. This image reveals a lot about the process and the reasons for the various phenomena seen. Firstly, it is immediately apparent that the “film” is not even close to a continuous layer, but instead seems to be made up of isolated agglomerations of small particles with large areas of bare substrate beneath them. This backs up the second explanation for the lack of intensity in the PXRD spectrum as the volume of material that the X-ray beam is passing through is very small thanks to the large gaps between the particles.

The size, shape and distribution of the particles reveals a lot about how they have formed. The particles are predominantly spherical in shape, between 1µm and 3µm in size and where they have agglomerated the interfacial cross-section is relatively small.

As described in Section 1.2.2, precursors can decompose in a variety of different ways in the AACVD process. The observations of this film indicate that the precursor is undergoing Process 4, whereby the precursor begins to decompose while still in the
Figure 6-11: SEM secondary electron image of material deposited from Compound 2 by AACVD.

gas phase, precipitating out as a solid.

This explains the extremely poor adhesion of the particles - they are essentially just sitting on the surface, having no chemical interaction whatsoever with it and can be removed with very little effort. This effect was demonstrated while imaging the samples using the SEM, often the electron beam would cause particles to move across the image or disappear entirely.

EDXS measurements were taken of the particles, the results of which are displayed in Table 6.5. From these measurements it is clear that the particles are not composed of a single material. Qualitatively, a mixture of CaCO$_3$ and CaS would explain the presence of all of the elemental signals, however as the film is not crystalline the assignment of specific compounds to these measurements is largely meaningless.

There is evidence in the SEM image of some of the precursor decomposing in a different way too. When probed by EDXS, the roughly circular darker areas of the substrate showed similar ratios of Ca, S, O and C to the particles, although the Si signal was much stronger. By contrast, the lighter areas of the substrate showed only the Si signal.

This suggests that these areas are evidence that some of the droplets of the precursor solution have reached the substrate before decomposing, forming a thin film of CaO and ultimately CaCO$_3$ in the areas that they have landed. However, the strength of the Si
Table 6.5: EDXS measurements of particles deposited from Compound 2 by AACVD.

Si signal omitted for clarity.

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<td>27.46</td>
</tr>
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<td>11</td>
<td>30.75</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>30.00</strong></td>
</tr>
</tbody>
</table>

Raman spectroscopy was also attempted on these samples, however extremely strong photoluminescence prevented any signals being picked up. An example of this is shown in Figure C-3. As described in Section 6.1 photoluminescence is a well understood phenomenon in doped CaS and so it is not surprising to see it here. Photoluminescence has also been observed in CaCO$_3$,$^{51}$ CaO$^{52}$ and CaSO$_4$,$^{53}$ so this information cannot be used to prove or disprove the presence of CaS in the material.

6.10 Further annealing of films

While a change was observed after the annealing of the material, there is no indication of whether it has reached an equilibrium state after just one hour of annealing. To test this, material deposited from AACVD of Compound 1 was analysed by PXRD once after deposition and annealing for one hour at 400°C and then analysed again after a second identical annealing step. The results of this experiment are shown in Figure 6-12.

There are few identifiable peaks in the pattern after the first annealing step and
very little information could be gained from that pattern alone. All of the peaks in
the first pattern are also present after the second annealing step, but sharper and with
greater intensity. Furthermore, after this second annealing step there are now more
peaks visible that could not be identified in the first pattern.

With these extra peaks the assignments of specific materials to the patterns becomes
possible. As seen in Figure 6-12 the peaks match the patterns of CaCO$_3$ and CaS,
indicating that these are the predominant compounds present in the material. This
information confirms and clarifies the observations of the previous section, that some
CaS is indeed produced by decomposition of calcium xanthates, however there is also
a large component of CaCO$_3$ as well, most likely thanks to formation of CaO during
decomposition followed by reaction with CO$_2$ either in the decomposition byproducts
or the ambient atmosphere.

As the calcium ion is already in its highest oxidation state it was possible to anneal
the material produced in a sulphur atmosphere without the risk of further oxidation.
An annealed film of material deposited from Compound 4 was subjected to a second
annealing step following the same procedure as before except for the inclusion of a boat
of elemental sulphur in the annealing tube. Once again, the PXRD pattern of the film
before and after annealing was compared and is shown in Figure 6-13.

This time, the intensity of the peaks in the pattern after the first annealing step was
much smaller. There appear to be a couple of very small peaks at around $2\theta = 31^\circ$ and
45° corresponding to the two most intense peaks in the bulk CaS pattern, however the
intensity is so low in this case that very little can be concluded from this.

After the second anneal in the sulphur atmosphere however there is a marked difference. The peaks are much more intense than anything seen previously and match well with the pattern for CaS. There is no evidence of CaCO₃ in this pattern. While there are some other very small peaks which have appeared, these were not able to be successfully assigned.

Figure 6-14 shows the film from Figure 6-9 one week after deposition and annealing had been performed. The necessity of some form of annealing step is made clear from the section of the film labelled c) which was intentionally left without annealing. The material in this area has begun to turn yellow (although this is unfortunately not very clear in the photograph), indicating that whatever intermediate is present after the initial deposition has begun to break down and potentially react with the air.

Figure 6-14: An image of the film deposited from Compound 4 (see Figure 6-9) after annealing steps and one week in ambient conditions. The sections were treated in the following ways: annealed in Ar a), annealed in Ar then S b), not annealed c), annealed in Ar d).
The annealed sections on the other hand have not visibly changed. The section annealed in the sulphur atmosphere appears more opaque than the areas immediately surrounding it which were not sulphur-annealed. This was the case immediately after the sulphur anneal was complete, but the reason for this is not clear.

6.11 Mixing of calcium and tin xanthate precursors

As previously described in Section 4.1.1, the alloying of CaS into SnS stabilises the rock salt phase of SnS and allows tuning of the band gap between 0.6 eV and 1.5 eV. In the previous section annealing in a sulphur atmosphere demonstrated that while the deposition of CaS from calcium xanthate precursors was not a straightforward process, it was possible to deposit CaS. An attempt was made to deposit a film from a solution containing both tin and calcium xanthates, along with the thioacetamide sulphur source found to be necessary for the formation of pure SnS (see Chapter 4).

The same procedure as that used in Section 4.9 was used again here (including thioacetamide). The only difference was that instead of making a 0.1 M solution of the tin xanthate precursor, the solution was instead 0.05 M tin xanthate precursor and 0.05 M Compound 3. Deposition continued as normal for the tin sulphide layers and there was no obvious visual difference between this film and SnS films made previously. The films appeared very uniform and smooth.

Figure 6-15 shows the PXRD pattern of the film created alongside the pattern of a film created using the same procedure without the calcium xanthate. All of the peaks in the pattern match those of \( \pi \)-SnS, with no indication of any other material present. The peaks in this pattern are significantly less intense than in the reference pattern. This is likely partly due to the fact that only half as much tin xanthate precursor was used, resulting in less material for the X-ray beam to interact with. This would appear to not entirely account for the loss in signal however, as the peaks are much less than half the intensity. Potentially the calcium xanthate may have had an inhibiting effect on the deposition of the tin xanthate.

The SEM image in Figure 6-16 gives a clear indication of the morphology of the film. The majority of the image displays a very uniform, practically featureless film. Dotted around the image are a few white spheroids of various sizes. These spheres are highly reminiscent of the ones seen in Figure 6-11. Images taken from other parts of the film showed the same morphology.

Table 6.6 details the results of EDXS measurements of the film. “Spot” measure-
Figure 6-15: PXRD pattern of a film deposited from equimolar tin and calcium xanthates. A previous film made from a purely tin xanthate precursor solution is included for comparison.

Figure 6-16: SEM image of a film deposited from equimolar Sn and Ca xanthates.
<table>
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<th>Measurement</th>
<th>Ca</th>
<th>Sn</th>
<th>S</th>
<th>O</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film</td>
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<td>-</td>
<td>53.23</td>
<td>46.77</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>2</td>
<td>-</td>
<td>53.15</td>
<td>46.85</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>3</td>
<td>-</td>
<td>50.31</td>
<td>49.69</td>
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<td></td>
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<td>10.84</td>
<td>12.45</td>
<td>18.37</td>
<td>43.19</td>
<td>15.14</td>
</tr>
</tbody>
</table>

Table 6.6: EDXS measurements from particles and areas of a film deposited from equimolar Sn and Ca xanthates. Si signals have been removed for clarity.

ments were taken of the spherical particles, along with area measurements of film the particles appear to be resting on. Examples of these types of measurements can also be seen in Figure 6-16. As can be seen from the table, the area measurements show no evidence whatsoever of the calcium xanthate’s decomposition products. As was seen in the previous chapter, these deposition conditions led to a tin sulphide film with a tin : sulphur ratio of almost 1:1 and a slight excess of tin.

The measurements of the particles on the other hand also show tin and sulphur, along with calcium, oxygen and carbon. The tin and sulphur content are again close to 1:1 but this time there is slightly more sulphur than tin. Taking into account the calcium, oxygen and carbon content as well suggests that the particles contain CaCO₃ and a sulphur-containing calcium compound. Based on the anomalously high oxygen content this may be CaSO₄, but without PXRD data to back this up it is impossible to be sure. CaSO₄ is also known to decompose at high temperature, making this unlikely.

All of this information leads to the conclusion that the presence of the calcium xanthate in the precursor solution does not significantly affect the outcome of the tin xanthate decomposition. The tin xanthate decomposes in much the same way as has been observed previously, leading to a compact film on the substrate.

The calcium xanthate’s behaviour also appears to be largely unaffected by the changes in deposition conditions. Once again it appears that the precursor begins to decompose in the gas phase, forming spherical particles which are then carried by the gas stream and potentially deposited on the surface. The sparse distribution of the particles can be attributed to the temperature of the deposition reaction - the deposition temperature was set at 200°C as was required for the deposition of the tin xanthate. As a result, the calcium containing particles were largely prevented from reaching the
heated part of the substrate.

In short, it appears that the two precursors have decomposed entirely independent of one another, the tin xanthate forming a continuous film on the surface and the calcium xanthate forming particles which then land on the surface later. There is no easy way to tell whether or not the particles contain tin sulphide as well. The measurements from the particles contained silicon signals as well as those displayed in Table 6.6, meaning that the electron beam is penetrating both the particle and any tin sulphide layer beneath to reach the silicon substrate. Therefore there is no way to tell where the tin and sulphur are in the volume that is being sampled by the electron beam. Considering that the precursor solution is expected to be homogeneous, it is expected that there would be some tin xanthate in the droplets too which would likely become trapped as the particle formed.

The calcium xanthate decomposition has been affected by the presence of the thiocetamide as evidenced by the increased sulphur content of the calcium containing particles. Unlike the tin containing film however there is still a large component of carbon and oxygen, indicating that the carbonate is still the predominant calcium containing material present. This indicates that calcium’s affinity for oxygen is significantly greater than that for sulphur, to the extent that it is very difficult to convert the deposited material to the desired sulphide.

6.12 Summary

In this chapter, a family of compounds based on the calcium ethyl xanthate system was synthesised and then characterised. The crystal structure was determined by single-crystal XRD and the effects of modification of the other ligands around the metal centre was investigated.

The decomposition of the compounds was investigated by TGA-MS and DSC. Multiple decomposition events were found, with the initial onset often below 100 °C but the final residual mass only being reached at around 400 °C. The most significant mass loss event was found to involve the rearrangement of the xanthate molecule, deinsertion of the chelating heterocumulene and loss of the spectator ligands around the metal centre. These findings would indicate that the intermediate product would be a metal alkoxide or thioalkane. The second smaller decomposition event was therefore expected involve loss of the alkyl group to result in the metal chalcogenide.

The residual mass of the products was too high to be a metal chalcogenide however
and further analysis of the product identified CaCO$_3$ as a major component of the product. This was expected to form either during the decomposition process through reaction with CO$_2$ generated from xanthate decomposition, or through later reaction with the atmosphere.

Attempts to deposit a film using the precursor instead resulted in the formation of particles while still in the vapour phase. This was described by Process 4 in Section 1.2.2. These particles appeared to be largely inert, settling on the substrate under the right conditions but not attaching in any way. Unless the deposition temperature was below 110°C very little of the material would settle on the heated substrate at all, due to what was thought to be convection currents set up near to the surface. Based on the findings from TGA this temperature would not be sufficient to access the final product and so a further annealing step was required to complete the process. Furthermore, as stated in Section 1.2.2 this is usually associated with the process temperature being too high, as the precursor is decomposing before even reaching the substrate. However, at a temperature of just 110°C this is pushing the lower limit of what can be achieved with the AACVD system used in this work.

The high levels of carbonate and oxide found in the product material were addressed by exposure to a sulphur atmosphere during annealing. This was found to significantly increase the CaS signal when analysed by PXRD, however it was clear that full conversion was not achieved and this did nothing to improve the morphology of the material.

An attempt was made to co-deposit the calcium precursors with the tin xanthate precursor investigated in the previous chapter, however the calcium xanthate continued to form solid particulates before reaching the substrate. This meant that it did not interact with the substrate or the tin sulphide film which was forming.

From this information it can be concluded that the decomposition pattern of calcium ethyl xanthates is likely not compatible with the AACVD technique. This is further exacerbated by the problem that like tin ethyl xanthate it does not decompose cleanly to form the metal sulphide, instead in this case forming a mixture of metal chalcogenides and carbonate. Unlike tin however, it is relatively resistant to substitution in a sulphur rich atmosphere, with incomplete conversion even after an hour at 400°C.

References


Chapter 7

Conclusions

The aim of this body of work was to develop new types of SnS solar cells based on alternative SnS phases - namely \( \pi \)-SnS and the rock salt phase. The first stage was to determine a suitable method by which the material could be deposited. The metal xanthate system was selected as a promising candidate for this purpose as it had previously been demonstrated to act as a clean, simple and safe precursor for the deposition of a wide variety of metal sulphides. In addition, thanks to the metal-sulphur bonds already present in the compound these acted as single-source precursors, needing no additional compounds to produce the desired material.

The tin(II) ethyl xanthate system was already documented and the crystal structure had been resolved. Two different routes to synthesis of the compound had been reported, both salt metathesis reactions, one in water and the other anhydrously in THF. Both methods were investigated in the course of this work, however the water-suspended method resulted in an impure product which was found to be very difficult to purify. Despite the added complexity of anhydrous air-sensitive synthesis the second method proved to be overall easier to perform, resulting in a clean product suitable for use in deposition reactions.

Tin(II) ethyl xanthate is not a particularly volatile compound and was observed to begin to break down even at relatively low temperatures, making it unsuitable for conventional CVD processes. Its good solubility in a variety of solvents made it an ideal candidate for aerosol-assisted CVD however and this deposition technique was adopted for the fabrication of thin films. This is the first recorded use of tin(II) xanthate as a precursor for the deposition of tin sulphide.

Surprisingly, the precursor did not cleanly form the metal sulphide as might be predicted from similar experiments with other metal xanthates. Instead the films appeared
to be almost entirely oxide, although in some cases some very small crystallites of the \( \pi \)-phase were detected. Thorough investigation of the entire process led to the conclusion that it was the precursor that was responsible for the formation of the oxide and not some form of contamination from elsewhere in the process.

At the cost of losing the compound’s value as a single source precursor, a reductive sulphur source was sought. A pair of related compounds, thioacetamide and thiourea, were evaluated. Both were found to effectively substitute the oxygen in the film for sulphur. Furthermore, the resulting films were pure, highly crystalline \( \pi \)-SnS. There are a few processes which have been demonstrated to form the \( \pi \)-phase, however as of the time of writing this is the lowest temperature vapour deposition process recorded. The films made with thiourea had improved morphology over those made with thioacetamide, appearing smoother and with fewer pinholes and so thiourea was used as the secondary sulphur source for subsequent experiments.

Searching the literature revealed that other than with CdS, no attempts had been made to form a heterojunction based on \( \pi \)-SnS. For this reason, it was necessary to screen a wide variety of candidate materials which had previously been shown to exhibit rectifying and photovoltaic behaviour when paired with \( \alpha \)-SnS or other photoactive layers to see whether an effective heterojunction could be formed. While a number of the resulting heterojunctions did show some sign of a diodic response, the device involving TiO\(_2\) was by far the most effective at producing a photocurrent. It is important to note here however that due to time constraints this set of experiments was not a complete and thorough analysis of each of these systems.

Experiments were conducted with a simple architecture which had recently been proven to be very effective for \( \alpha \)-SnS, however no positive results were achieved. An attempt was also made to use the SnS layer as a p-type contact layer for MAPbI\(_3\), and while an appreciable photocurrent (up to 5.3 mA cm\(^{-2}\), giving an efficiency of 1.9\%) was generated the performance of the cells was still quite poor. It should be noted however that such a combination of layers has not been attempted before and these results were obtained from non-optimised cells.

Following the findings of a report on the alloying of SnS with various alkaline earth metal sulphides through PLD, an attempt was made to see whether the same effect could be achieved using a chemical deposition technique. Calcium was the alkaline earth metal of choice based on the findings of the report.

To avoid disrupting the decomposition chemistry a system equivalent to that of the
tin ethyl xanthate was realised for calcium. This involved the use of the same ethyl xanthate ligand, however a set of spectator ligands was required in order to satisfy calcium's co-ordination sphere. To this end, six entirely new compounds were synthesised and characterised, each based on a calcium ethyl xanthate core with a different set of spectator ligands occupying the rest of the positions. The properties of these compounds was probed and their decomposition behaviour was examined.

Unfortunately, similar issues to those found in the tin system also plagued the calcium system, with the oxide being formed in preference to the sulphide. This was followed by subsequent reaction with CO$_2$ to form the carbonate.

As calcium has no higher oxidation state it was possible to directly anneal the resulting material in a sulphur atmosphere. While this did result in substitution of oxygen and carbonate anions for sulphur and an increased sulphide content, total conversion was not achieved and a suitable set of deposition conditions was not identified for this precursor system.

Further development of this work should focus on three main areas. First of all while a successful route to $\pi$-SnS was developed, the pursuit of this goal highlighted that understanding of the metal xanthate decomposition reaction is far from complete. Many of the systems which have been explored previously have proven successful in the facile deposition of a pure metal sulphide film and through various means a number of reasonable mechanisms for decomposition have been suggested. However, it is clear that there is more to the story than a single, simple mechanism which can be used to account for all metal xanthate decomposition.

In order to unpick this, a variety of different techniques would need to be employed to study the system during decomposition from different vantage points. It would be necessary for the techniques used to be able to collect time-resolved measurements of the reaction, allowing the various intermediates to be probed in situ. Flow NMR could be used to monitor the hydrogen environments present in the various ligands to determine how the compound fragments and at what temperature. Powder X-ray diffraction measurements could be conducted on a sample of the precursor immobilised on a heated stage, allowing for crystal phases to be analysed as they appear and disappear in the bulk compound.

A good deal of mass spectrometry has already been conducted to try to tease apart the various processes occurring during the decomposition reaction, both in this work and in the literature. Despite this there are still many unanswered questions and the evi-
evidence suggests that the mechanism may be strongly dependent upon the identity of the metal centre. Ideally, to fully characterise the assortment of gaseous by-products produced during the reaction, the temperature would be raised very slowly and the exhaust gases would be passed through a gas chromatography column to separate them. A combination of gas-chromatography mass spectrometry (GCMS) and inductively coupled plasma mass spectrometry (ICPMS) could be used to analyse these gases. The GCMS gives information on the chemical structure of the gases, while the ICPMS easily identifies the type and ratios of the elements involved.

The second key focus is the realisation of a solar cell architecture that works well with $\pi$-SnS. The properties of $\pi$-SnS indicate that it should perform well as an absorber material, however to do this it must be paired with the correct materials to give interfaces with good charge transfer, a high recombination resistance and efficient charge separation.

The first step of this would be to fully characterise the material to understand as much as possible about its photovoltaic behaviour. This would be done by performing electrochemical measurements to determine its oxidation and reduction potentials, Mott-Schottky measurements to determine the carrier density and flat-band potential and chopped photocurrent measurements to learn more about its photovoltaic response.

The next step would be to identify the best candidate materials to build a device using the $\pi$-SnS as the photoabsorber. This work has only scratched the very surface here. A full screening would need to consider many different materials that have already been proven for photovoltaic applications based on the information gathered from the experiments mentioned above. Each of these would need to be independently tested and optimised for performance in the cell. The fact that a photocurrent was detected in at least some of the devices made indicates that there is promise even just in the materials tested. With more time and effort each step of the process could be optimised and the cell performance could undoubtedly be significantly improved.

Having done this the device as a whole (and sections thereof) should also be thoroughly characterised. Device performance measurements were performed in this work, namely J-V curves from which the $V_{OC}$, $J_{SC}$, fill factor and power conversion efficiency can be extracted. There are however a host of other measurements that are required to fully understand the processes occurring in a complete device. Electrochemical impedance spectroscopy (EIS) can help model and understand the effects of the various interfaces within the device, as well as the providing information about the series re-
istance and other phenomena occurring within the cell. External quantum efficiency (EQE) measurements are an important consideration to determine the spectral response of the cell and identify losses that are non-uniform across the energy spectrum.

The final area of focus would be the SnS-CaS (or other alkaline earth metal) alloy material. The combination of these materials had already been proven to stabilise a rock salt structure for SnS, otherwise only accessible at high temperature. Furthermore this gave the opportunity to tune the band gap of the material across a relatively broad range, encompassing much of the range of optimum energies for maximum conversion efficiency.

Attempts to use the precursors developed in the course of the work for deposition of CaS were not successful and so a process for the co-deposition of SnS and CaS could not be developed. This proved again to be an unexpected limitation of the xanthate system, but whether or not the issues encountered could be overcome was not determined satisfactorily.

If a set of process conditions could not be found which produces the desired material cleanly, the next step would be to modify the precursor to see if analogous compounds would give a more favourable result. This could be done firstly by modifying the spectator ligands and the R- group on the xanthate, however if this also fails the next step would be to try xanthate analogues, i.e. dithiocarbamates and trithiocarbonates. Dithiocarbamates have already been investigated as potential metal sulphide precursors, although they generally need higher deposition temperatures than xanthates. The potential for metal trithiocarbonates to deposit metal sulphides is as of the time of writing almost entirely unexplored.

While the deposition of the mixed metal sulphide by chemical means would be an entirely novel feat in its own right, the resulting material has not yet been incorporated into a solar cell either, despite the fact that it has successfully been synthesised as a thin film. Echoing the previous focus, the same process of material characterisation, screening for and optimisation of cell architecture and device evaluation would also be required for this material.

Given that the mixed metal sulphide has already shown encouraging properties as a solar absorber material, realisation of such a device could usher in an entirely new, high-efficiency, low-cost solar technology.
Appendix A

Crystallographic Information
Figure A-1: Bond length analysis associated with changes in supporting ligands.
### Table A.1: Bond angle analysis for Compound 2

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<td>N31-Ca-N32</td>
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*Average values:* 11.3 11.7
Figure A-2: Compound 1, \([\text{Ca(S}_2\text{COEt})_3\text{(OEt)}_3]\).
Table 1. Crystal data and structure refinement for e16alj02.

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<td>Space group</td>
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<td></td>
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<td>Largest diff. peak and hole</td>
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Figure A-3: Compound 2, [Ca(S_2COEt)_2(pmdeta)].
Table 1. Crystal data and structure refinement for e16alj05.

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<td>Max. and min. transmission</td>
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Figure A-4: Compound 3, $[\text{Ca(S}_2\text{COEt)}_2(\text{py})_3]$. 
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<td>b</td>
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<td>β</td>
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<tr>
<td>c</td>
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Figure A-5: Compound 4, $\text{[Ca(S}_2\text{COEt})_2(3-\text{mepy})_3]}$. 
Table 1. Crystal data and structure refinement for s16alj26.

Identification code s16alj26
Empirical formula C24 H31 Ca N3 O2 S4
Formula weight 561.84
Temperature 150.00(10) K
Wavelength 1.54184 Å
Crystal system Triclinic
Space group P-1
Unit cell dimensions
\[ a = 8.7081(3) \, \text{Å} \quad \alpha = 100.256(3)^\circ. \]
\[ b = 11.1043(3) \, \text{Å} \quad \beta = 100.522(3)^\circ. \]
\[ c = 17.1306(5) \, \text{Å} \quad \gamma = 110.428(3)^\circ. \]
Volume 1472.72(8) Å³
Z 2
Density (calculated) 1.267 Mg/m³
Absorption coefficient 4.683 mm⁻¹
F(000) 592
Crystal size 0.250 x 0.150 x 0.100 mm³
Theta range for data collection 4.403 to 73.477°.
Index ranges -10<=h<=10, -13<=k<=12, -20<=l<=20
Reflections collected 10972
Independent reflections 5777 [R(int) = 0.0223]
Completeness to theta = 67.684° 99.7 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 1.00000 and 0.66917
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 5777 / 41 / 386
Goodness-of-fit on F² 1.060
Final R indices [I>2sigma(I)] R1 = 0.0396, wR2 = 0.1019
R indices (all data) R1 = 0.0423, wR2 = 0.1046
Extinction coefficient n/a
Largest diff. peak and hole 1.173 and -0.431 e.Å⁻³
Figure A-6: Compound 5, $[\text{Ca}(_2\text{COEt})_2(4\text{-mpy})_3]$. 
Table 1. Crystal data and structure refinement for s16alj27.

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<td>b = 21.8577(6) Å</td>
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<td>c = 16.4596(6) Å</td>
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Figure A-7: Compound 6, [Ca(S₂COEt)₂(4-dmap)₃].
Table 1. Crystal data and structure refinement for e16alj11.

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Appendix B

NMR spectra

Figure B-1: $^1$H NMR of Sn(S$_2$COEt)$_2$. 
Figure B-2: $^{13}$C NMR of $\text{Sn(S}_2\text{COEt)}_2$.

Figure B-3: $^{119}$Sn NMR of $\text{Sn(S}_2\text{COEt)}_2$. 
Figure B-4: $^1$H NMR of $[\text{Ca(S}_2\text{COEt)}_2\text{(OHEt)}_3]$, Compound 1 in benzene.

Figure B-5: $^{13}$C NMR of $[\text{Ca(S}_2\text{COEt)}_2\text{(OHEt)}_3]$, Compound 1 in benzene.
Figure B-6: $^1$H NMR of $[\text{Ca}(\text{S}_2\text{COEt})_2(\text{pmdeta})]$, Compound 2 in benzene.

Figure B-7: $^{13}$C NMR of $[\text{Ca}(\text{S}_2\text{COEt})_2(\text{pmdeta})]$, Compound 2 in benzene.
Figure B-8: $^1$H NMR of $[\text{Ca(S}_2\text{COEt)}_2\text{(py)}_3]$, Compound 3 in benzene.

Figure B-9: $^{13}$C NMR of $[\text{Ca(S}_2\text{COEt)}_2\text{(py)}_3]$, Compound 3 in benzene.
Figure B-10: $^1$H NMR of [Ca(S$_2$COEt)$_2$(3–mpy)$_3$], Compound 4 in benzene.

Figure B-11: $^{13}$C NMR of [Ca(S$_2$COEt)$_2$(3–mpy)$_3$], Compound 4 in benzene.
Figure B-12: $^1$H NMR of $[\text{Ca}(\text{S}_2\text{COEt})_2(\text{4-mpy})_3]$, Compound 5 in benzene.

Figure B-13: $^{13}$C NMR of $[\text{Ca}(\text{S}_2\text{COEt})_2(\text{4-mpy})_3]$, Compound 5 in benzene.
Figure B-14: $^1$H NMR of $[\text{Ca(S}_2\text{COEt)}_2(4-\text{dmap})_3]$, Compound 6 in benzene.

Figure B-15: $^{13}$C NMR of $[\text{Ca(S}_2\text{COEt)}_2(4-\text{dmap})_3]$, Compound 6 in benzene.
Appendix C

Supplementary information

C.1 Figures

Figure C-1: A comparison of the PXRD patterns collected from films deposited on silicon and glass in the same reaction. The precursor solution used was 1:1 Sn(S$_2$COEt)$_2$ : thioacetamide.
Figure C-2: Tauc plots for direct allowed (a), indirect allowed (b), direct forbidden (c) and indirect forbidden (d) transitions generated from UV/vis measurements of π-SnS thin films.
Figure C-3: An example of the strong photoluminescent response seen in Raman spectra of the films deposited from the calcium xanthate precursors.

Figure C-4: Concurrent thermo-gravimetric and mass spectrum analysis of Compound 1 (EtOH).
Figure C-5: Concurrent thermo-gravimetric and mass spectrum analysis of Compound 2 (pmdeta).

Figure C-6: Concurrent thermo-gravimetric and mass spectrum analysis of Compound 3 (py).
Figure C-7: Concurrent thermo-gravimetric and mass spectrum analysis of Compound 4 (3mpy).

Figure C-8: Concurrent thermo-gravimetric and mass spectrum analysis of Compound 5 (4mpy).
Figure C-9: Concurrent thermo-gravimetric and mass spectrum analysis of Compound 6 (4dmap).
C.2 Tables
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Table C.1: Parameters used for attempts at AACVD deposition of CaS. This table is continued overleaf.
Table C.2: Parameters used for attempts at AACVD deposition of CaS. Table continued from the previous page.

In this experiment a seed layer was deposited at 100°C and then annealed at 400°C.

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Sample Temp. (°C) | Gas pressure (psi) | Compound Solvent Film? | Anneal atmosphere | CaS?