$N$-methyl-$N'$, $N'$-dimethylethylene-/propylene-diaminodithiocarbamato-metal complexes as single source precursors for metal sulfide semiconductors materials.

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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AACVD</td>
<td>aerosol-assisted chemical vapour deposition</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>MOCVD</td>
<td>metal-organic chemical vapour deposition</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl group</td>
</tr>
<tr>
<td>iPr</td>
<td>i-propyl group</td>
</tr>
<tr>
<td>Me</td>
<td>methyl group</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl group</td>
</tr>
<tr>
<td>tBu</td>
<td>t-butyl group</td>
</tr>
<tr>
<td>Eg</td>
<td>band gap</td>
</tr>
<tr>
<td>EDAX</td>
<td>energy dispersive X-ray analysis</td>
</tr>
<tr>
<td>JCPDS</td>
<td>joint committee of powder diffraction standard</td>
</tr>
<tr>
<td>LED</td>
<td>light emitting diod</td>
</tr>
<tr>
<td>MS</td>
<td>mass spectroscopy</td>
</tr>
<tr>
<td>mmol</td>
<td>millimol</td>
</tr>
<tr>
<td>m.p</td>
<td>melting point</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>ppm</td>
<td>part per million</td>
</tr>
<tr>
<td>sccm</td>
<td>standard cubic centimetres per minute</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>p-XRD</td>
<td>powder X-ray diffraction</td>
</tr>
<tr>
<td>SSP</td>
<td>single source precursor</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>UV/Vis</td>
<td>ultra-violet/visible</td>
</tr>
</tbody>
</table>
Summary

A series of N-methyl-N’,N’-dimethylethylene-/propylene-diaminodithiocarbamato-metal complexes \([M(S_2CN(Me)(CH_2)_nN(Me)_2)_2]\) (\(M = Zn, Cd, Cu, Ni; \ n = 2 \text{ or } 3\)), \([M(S_2CN(Me)(CH_2)_nN(Me)_2)_3]\) (\(M = Co, In; \ n = 2 \text{ or } 3\)), \([M(S_2CN(Me)(CH_2)_nN(Me)_2)]\) (\(M = Ag; \ n = 3\)) has been synthesized and characterised by microelemental analysis, NMR \((^1H, ^{13}C)\), IR and some by X-ray crystallography. X-ray single crystal structures for \([M(S_2CN(Me)(CH_2)_nN(Me)_2)_2]\) (\(M = Zn, Cd, n = 2 \text{ or } 3\)) and \([M(S_2CN(Me)(CH_2)_nN(Me)_2)_3]\) (\(M = In; \ n = 2 \text{ or } 3\)) have been determined. Zinc and cadmium structures are polymers. All polymerise through the nitrogen of dimethylamino group to the metal atoms. Both indium structures are monomers where each indium is bonded with six sulphur atoms from three bidentate dithiocarbamato ligands.

All twelve metal complexes were solids and stable to air and moisture for periods of several months hence potentially useful as single source precursor for metal sulfide thin films. Metal sulfide thin films including zinc sulfide, cadmium sulfide, copper sulfide, nickel sulfide, cobalt sulfide, indium sulfide, copper indium sulfide, silver indium sulfide, and cadmium zinc sulfide were deposited by aerosol assisted chemical vapour deposition (AACVD) method. Deposition from each precursor was carried out at three different (300, 400 and 500 °C) temperatures to investigate the effect of deposition temperature on the size and shape of crystallites as well as phase of the material. All deposited films were characterized by powder X-ray diffraction (p-XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and atomic force microscopy (AFM). Mostly good quality, adhesive and specular thin films of these materials were obtained. p-XRD showed significant changes in the phase of materials depending upon the growth temperature. SEM and AFM images showed the morphology of the films was strongly linked to the deposition temperature. This is the first systematic study on N-methyl-N’,N’-dimethylethylene-/propylene-diaminodithiocarbamatometal complexes and their use as single source precursors for the metal sulfide thin films.
Declaration

I hereby declare that no portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of the University of Manchester or any other university or other institute of learning.

Yousef Alghamdi
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I am thankful to my supervisor Professor Paul O’Brien for his patience and guidance to complete my doctoral degree. I would like to thank Dr. M. Azad Malik for his discussions and valuable guidance and comments through out my PhD period especially during writing up of my thesis. My thanks are also due to Masood Akhtar and Ahmed Abdul Alhady.

My special thanks to Ms. Judith Shackleton, Mr. Mike Faulkner, Mr. Alan Harvey, Andrew Forrest for training me in XRD, SEM, and AFM and James Raftery and Madeleine Helliwell for solving the crystal structures.

Last but not the least my very special thanks and love to my mother and my wife and daughters for their support throughout my PhD research.
Dedication

To my uncle Yousef
Chapter 1: General Introduction
1.1 Classification of solids
Solid materials can be classified into three categories based on their conductivity: conductor, semiconductor, and insulator. According to the band theory, difference between conductors, insulators and semiconductors can be visualized by plotting the available energies for electrons in the materials. Instead of having discrete energies as in the case of free atoms, the available energy states form bands.

1.2 Semiconductors
The conductivity value of semiconductors ($10^4$ to $10^8$ Ω cm$^{-1}$) lies between the conductivity value of metals ($10^8$ to $10^4$ Ω cm$^{-1}$) and insulators (less than $10^8$ Ω cm$^{-1}$). In semiconductors, at room temperature, very few electrons gain enough thermal energy to jump the energy gap from the valence band to conduction band, which is necessary for electrons (or holes) to be available for electric current conduction. For this reason, pure semiconductors and insulators in the absence of applied electric field, have roughly similar resistance. In insulators the electrons in the valence band are separated by a large gap from the conduction band, in conductors the valence band overlaps the conduction band, and in semiconductors there is a small enough gap between the valence and conduction bands that thermal or other excitations can bridge the gap.

Another possibility of defining a semiconductor is through the free carrier concentration at room temperature. Semiconductors have moderate carrier density while conductors have rather large carrier density, and insulators have a negligible carrier density. Table 1-1 summarizes the classification according to different criteria: conductivity, energy gap, and carrier density.
Table 1-1: Classification of solids according to their conductivities (\(\sigma\)), energy gap \(E_G\) and carrier density \(n\) at room temperature \(^{1a}\)

<table>
<thead>
<tr>
<th>Type of Solid</th>
<th>(\sigma) (cm(^{-1}))</th>
<th>(E_G) (eV)</th>
<th>(n) (cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal</td>
<td>(10^5 - 10^{10})</td>
<td>No energy gap</td>
<td>(10^{22})</td>
</tr>
<tr>
<td>Semimetal</td>
<td>(10^2 - 10^5)</td>
<td>(E_G \leq 0)</td>
<td>(10^{17} - 10^{21})</td>
</tr>
<tr>
<td>Semiconductor</td>
<td>(10^{-9} - 10^{-2})</td>
<td>(0 &lt; E_G &lt; 4)</td>
<td>(&lt; 10^{17})</td>
</tr>
<tr>
<td>Insulator</td>
<td>(&lt; 10^{-9})</td>
<td>(4 \leq E_G)</td>
<td>(&lt; &lt; 1)</td>
</tr>
</tbody>
</table>

1.2.1 Band Structure

The band structure of a solid describes ranges of energy that an electron is "forbidden" or "allowed" to have. It is due to the diffraction of the quantum mechanical electron waves in the periodic crystal lattice. The band structure of a material determines several characteristics, in particular its electronic and optical properties. The electrons of a single free-standing atom occupy atomic orbitals, which form a discrete set of energy levels. If several atoms are brought together into a molecule, their atomic orbitals split, as in a coupled oscillation. This produces a number of molecular orbitals proportional to the number of atoms. When a large number of atoms (of order \(10^{20}\) or more) are brought together to form a solid, the number of orbitals becomes exceedingly large, and the difference in energy between them becomes very small, so the levels may be considered to form continuous bands of energy rather than the discrete energy levels of the atoms in isolation. However, some intervals of energy contain no orbitals, no matter how many atoms are aggregated, forming bandgap.
1.2.2 Band structure in different types of solids

Figure 1-1: Simplified diagram of the electronic band structure of metals, semiconductors and insulators.

Metals contain a band that is partly filled and partly empty regardless of temperature. Therefore they have very high conductivity. The lowermost, almost fully occupied band in an insulator or semiconductor is called the valence band by analogy with the valence electrons of individual atoms. The uppermost, almost unoccupied band is called the conduction band because only when electrons are excited to the conduction band can current flow in these materials. The difference between insulators and semiconductors is only that the forbidden bandgap between the valence band and conduction band is larger in an insulator (Figure 1.1), generally upwards of 4 eV. So that fewer electrons are found there and the electrical conductivity is lower. Whilst, semiconductors have bandgap of somewhat less than 4 eV and often within the range of IR-Vis-UV region. One of the main mechanisms for electrons to be excited to the conduction band is due to thermal energy.

1.2.3 Intrinsic and extrinsic semiconductors

The conductivity of semiconductors is not only affected by temperature but is also changed by the level of impurities and defects in crystal lattice. An intrinsic
semiconductor is also called undoped semiconductor containing no dopant atoms. The property of electrical conductivity can be due to crystal lattice defect or thermal excitation. In an intrinsic semiconductor number of electrons and holes created by excitation of electron is equal \( n = p \). Examples of intrinsic semiconductors include elemental semiconductors, such as Si and Ge, and compound semiconductors of two or more elements, like CdS, GaAs or CuInS\(_2\). An extrinsic semiconductor is a semiconductor that has been doped. Doping involves adding dopant atoms to an intrinsic semiconductor, which changes the electron and hole carrier concentrations of the semiconductor at thermal equilibrium. During doping, impurity atoms are introduced to an intrinsic semiconductor. Impurity atoms are atoms of an element different from the intrinsic semiconductor atoms. Impurity atoms act as either donors or acceptors to the intrinsic semiconductor, changing the electron and hole concentrations of the semiconductor. Impurity atoms are classified as donor or acceptor atoms based on the effect they have on the intrinsic semiconductor. Donor impurity atoms have more valence electrons than the atoms they replace in the intrinsic semiconductor lattice. Donor impurities "donate" their extra valence electrons to a semiconductor's conduction band, providing excess electrons to the intrinsic semiconductor. Excess electrons increase the electron carrier concentration \( n_0 \) of the semiconductor, making it n-type. Acceptor impurity atoms have fewer valences electron than the atoms they replace in the intrinsic semiconductor. They "accept" electrons from the semiconductor's valence band. This provides excess holes to the intrinsic semiconductor. Excess holes increase the hole carrier concentration \( p_0 \) of the semiconductor, creating a p-type semiconductor.

### 1.2.3.1 N-type doping

An example of n-type doping is arsenic in silicon. Arsenic has five valence electrons whereas silicon has four; there is one additional electron. This extra electron creates donor electron levels just below the conduction band (Figure 1-2). Thermal excitation can causes electrons to move from the new donor levels (rather than the valence band) into the conduction band. The donor levels do not display band-like qualities and electrons are not free to move. Conduction is caused by movement of the promoted electrons in the partially filled conduction band. Due to the proximity of donor levels
and the conduction band, electrons can move from one to the other more easily than in pure silicon material.

![Diagram of Electronic Energy Levels](image)

Figure 1-2: The result of n-type doping on band structure

The bandgap for silicon is 1.1eV whereas for arsenic doped silicon the donor level energy is less than 0.1eV below the conduction band. Lesser thermal energy is required for arsenic doped silicon to reach the same conductivity level as pure silicon.

1.2.3.2 P-type doping

![Diagram of Electronic Energy Levels](image)

Figure 1-3: The result of p-type doping on band structure.

An example of p-type doping is gallium in silicon. Gallium has three valence electrons whereas silicon has four. The resulting material is therefore deficient by one electron. Accepter levels form just above the valence band. Thermal excitation causes electrons to move from the valence band to the new acceptor levels (rather than to the
conduction band). Similar to the donor levels in n-type materials, the acceptor levels in p-type materials do not display band-like qualities and electrons are not free to move (i.e. they are localized energy levels). The movement of electrons from the valence band to the acceptor levels causes positively charged holes to be left behind in the valence band (Figure 1-3). The movement of these holes in the valence band causes the conduction of the material. Due to the proximity of the valence band and acceptor levels, electrons can move from one to the other more easily than in the pure silicon. In gallium doped silicon the acceptor level energy is \( \sim 0.1 \) eV above the valence band (compared to the 1.1 eV bandgap of silicon)

### 1.2.4 P-N Junction

The most important property of semiconductor is the formation of the P-N junction. When p-type and n-type materials are placed in contact with each other, the junction behaves very differently than either type of material alone. Specifically, current will flow readily in one direction (forward biased) but not in the other (reverse biased). This non-reversing behaviour arises from the nature of the charge transport process in the two types of materials (Figure 1-4).

For a p-n junction at equilibrium, the Fermi levels match on the two sides of the junctions. Electrons and holes reach an equilibrium at the junction and form a depletion region. The upward direction in the diagram represents increasing electron energy. Energy needs to be supplied, in order to get an electron to go up, one level, and a hole to go down, as in diagram Figure 1-4 (a). To reverse-bias the p-n junction, the p side is made more negative, making it "uphill" for electrons moving across the junction. The conduction direction for electrons in the diagram is right to left, and the upward direction represents increasing electron energy. To forward bias the p-n junction, the p side is made more positive, so that it is "downhill" for electron motion across the junction. An electron can move across the junction and fill a vacancy or "hole" near the junction. It can then move from vacancy to vacancy leftward toward the positive terminal, which could be described as the hole moving right. The conduction direction for electrons in the diagram is right to left, and the upward direction represents increasing electron energy. When the p-n junction is forward biased, the electrons in the n-type material which have been elevated to the
conduction band and which have diffused across the junction find themselves at a higher energy than the holes in the p-type material. They readily combine with those holes, making possible a continuous forward current through the junction.

Figure 1-4: Simple band gap diagrams of p-n junction at (a) equilibrium (b) reverse bias (c) forward bias.

1.2.5 Direct and indirect semiconductors

Direct bandgap semiconductors, *i.e.* semiconductors for which the minimum of the conduction band occurs at the same wavevector, *k*, as the maximum of the valence band, have a stronger absorption of light as characterized by a larger absorption coefficient. They are also the favoured semiconductors when fabricating light emitting devices. Indirect bandgap semiconductors, *i.e.* semiconductors for which the minimum of the conduction band does not occur at the same wavevector as the maximum of the valence band, are known to have a smaller absorption coefficient and
are rarely used in light emitting devices. The difference between direct and indirect transitions is represented in Figure 1-5.

For a direct bandgap semiconductor the minimum value of energy $E(k)$ in the conduction band and maximum value of $E(k)$ in the valence band coincide at the same value of $K$. In an indirect bandgap semiconductor like silicon, an electron cannot be directly excited to the conduction band with energy $E_g$. Additional energy is required as a phonon, the electron undergoes a change in momentum and we obtain an indirect transition with energy $h\nu = E_g + E_{phonon}$. The phonon energy, $E_{ph}$, is very small compared to $E_g$.

![Diagram of E-k diagram illustrating photon absorption in a direct band gap semiconductor and indirect band gap semiconductor.](image)

Figure 1-5: E-k diagram illustrating (a) photon absorption in a direct band gap semiconductor (b) photon absorption in a indirect band gap semiconductor.

Indirect transitions require the participation of phonons (lattice vibrational energy) and hence are explicitly dependent on temperature. The absorption coefficient for indirect semiconductors is smaller than for direct semiconductors, in essence light absorption is a less efficient process for indirect semiconductors. For simplicity we have considered these fundamental absorption processes for direct and indirect semiconductors, *i.e.* those that occur for light photon of energies similar to the bandgap energy.
Since the absorption process in an indirect bandgap semiconductor involves a phonon in addition to the electron and photon, the probability of having an interaction take place involving all three particles will be lower than a simple electron-photon interaction in a direct bandgap semiconductor. As a result absorption is much stronger in a direct bandgap material.

Similarly, in the case of light emission, a direct bandgap material is also more likely to emit a photon than an indirect bandgap material. While indirect bandgap materials are occasionally used for some LEDs, they result in a low conversion efficiency. Direct bandgap materials are used exclusively for semiconductor laser diodes. Some common semiconductors are presented in Figure 1-2. 

1b
Table 1-2: Properties of some common semiconductors<sup>1b</sup>.

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Structure</th>
<th>Lattice Parameters (Å)</th>
<th>Band-gap (eV)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV-IV</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>Cubic</td>
<td>5.646</td>
<td>0.66</td>
<td>Indirect</td>
</tr>
<tr>
<td>Si</td>
<td>Cubic</td>
<td>5.437</td>
<td>1.12</td>
<td>Indirect</td>
</tr>
<tr>
<td>II-VI</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnS</td>
<td>Cubic hexagonal</td>
<td>5.420</td>
<td>3.68</td>
<td>Direct</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.820, 6.260</td>
<td>3.91</td>
<td>Direct</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.832</td>
<td>2.42</td>
<td>Direct</td>
</tr>
<tr>
<td>CdS</td>
<td>Cubic hexagonal</td>
<td>4.140, 6.710</td>
<td>2.51</td>
<td>Direct</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.669</td>
<td>2.70</td>
<td>Direct</td>
</tr>
<tr>
<td>ZnSe</td>
<td>Cubic hexagonal</td>
<td>4.000, 6.540</td>
<td></td>
<td>Direct</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.050</td>
<td>1.70</td>
<td>Direct</td>
</tr>
<tr>
<td>CdSe</td>
<td>Cubic hexagonal</td>
<td>4.300, 7.010</td>
<td>1.75</td>
<td>Direct</td>
</tr>
<tr>
<td>CdTe</td>
<td>Cubic</td>
<td>6.482</td>
<td>1.56</td>
<td>Direct</td>
</tr>
<tr>
<td>III-V</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GaP</td>
<td>Cubic</td>
<td>5.451</td>
<td>2.26</td>
<td>Indirect</td>
</tr>
<tr>
<td>GaAs</td>
<td>Cubic</td>
<td>5.653</td>
<td>1.42</td>
<td>Direct</td>
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<tr>
<td>InP</td>
<td>Cubic</td>
<td>5.869</td>
<td>1.35</td>
<td>Direct</td>
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<td>InAs</td>
<td>Cubic</td>
<td>6.058</td>
<td>0.36</td>
<td>Direct</td>
</tr>
<tr>
<td>AlAs</td>
<td>Cubic</td>
<td>5.661</td>
<td>2.16</td>
<td>Indirect</td>
</tr>
</tbody>
</table>
1.2.6 **Classification and applications of semiconductors**

Semiconductor materials can be classified based on their constituents and properties. Table 1-3\textsuperscript{1c} lists some of the semiconductors with their applications.

Table 1-3: Classification and applications of semiconductors\textsuperscript{1c}

<table>
<thead>
<tr>
<th>Type</th>
<th>Example</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV semiconductors</td>
<td>Si, Ge, Diamond</td>
<td>Microchips, solar cells</td>
</tr>
<tr>
<td>IV- IV</td>
<td>SiC, SiGe</td>
<td>Lightning arrestors, blue LED, Schottky</td>
</tr>
<tr>
<td>Semiconductors</td>
<td></td>
<td>Light emitting diodes</td>
</tr>
<tr>
<td>III-V</td>
<td>AlN, AlAs, AlP, BN, BP, BAs, GaSb, GaAs, GaN, GaP, InSb, InSb, InN, InP, AlGaAs, InGaAs, InGaP, AlInAs, AlInSb, GaAsP, AlGaN, AlGaP, InGaN, InAsSb, InGaSb, GaInNAsSb, CdSe, CdS, CdTe, ZnO, ZnSe, ZnS, ZnTe, CdZnTe, HgCdTe, HgZnTe, HgZnSe, PbSe, PbS, PbTe, SnS, SnTe, CdP, Cd$_3$As$_2$, Cd$_3$Sb$_2$, ZnP, Zn$_3$As$_2$, Zn$_3$Sb$_2</td>
<td>IR photo detectors, red emitting diodes, solar cells, Light emitting diodes, Solar cells, Solid state lasers, IR detectors, Thermal imaging, IR detectors, magneto resistors</td>
</tr>
<tr>
<td>Ternary semiconductor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II-V</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV-VI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Semiconductors</td>
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<td></td>
</tr>
<tr>
<td>II-V</td>
<td></td>
<td></td>
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<tr>
<td>Semiconductors</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{1c} Reference or note for Table 1-3.
1.3 Deposition of thin film semiconductor materials

Semiconductor thin films can be prepared by various techniques including: Deposition, Removal, Patterning and modification of electrical properties

Deposition: Deposition is a process that grows, coats or transfers a material onto the substrate: e.g., Physical Vapour Deposition (PVD), Chemical Vapour Deposition (CVD), Electro Chemical Deposition (ECD), Molecular Beam Epitaxy (MBE), Atomic Layer Deposition (ALD), and Chemical Bath Deposition (CBD).

Removal: Removal processes are any that remove material from the wafer either in bulk or selective form. These include etching and chemical-mechanical methods.

Patterning: The series of processes that shape or alter the existing shape of deposited materials and are generally referred to as lithography.

Modification of electrical properties: The process consisting of doping transistor sources and drains originally by diffusion furnaces and later by ion implantation.

1.3.1 Chemical vapour deposition (CVD)

Chemical vapour deposition is a chemical process used to produce high purity and high performance thin film materials. In a typical CVD process the substance is exposed to one or more precursors which react and/or decompose on the surface of the substrate at higher temperature to produce the desired material.

1.3.1.1 Types of CVD

There are a number of CVD methods which differ in the means by which chemical reactions are initiated (activation process) and process condition. These include:
Atmospheric pressure CVD (AP-CVD) – CVD process at atmospheric pressure.
Low-pressure CVD (LP-CVD) – CVD process at low pressures. Reduced pressure tends to reduce unwanted gas-phase reactions and improves film uniformity across the wafer.
Aerosol assisted CVD (AA-CVD) – CVD process in which the precursors are transported to the substrate by means of a liquid/gas aerosol, which can be generated ultrasonically. This technique does not require volatile precursors.
Direct liquid injection CVD (DLI-CVD) – CVD process in which the precursors are in liquid form. Liquid solutions are injected in a vapourization chamber towards reactors. Then
the precursor vapours are transported to the substrate as in classical CVD process. This technique is suitable for use on liquid or solid precursors. High growth rates can be reached using this technique. **Plasma – Enhanced CVD (PE-CVD)** – CVD process that utilize plasma to enhance chemical reaction rates of the precursors. PECVD processing allows deposition at lower temperatures, which is often critical in the manufacture of semiconductors. **Remote plasma-enhanced CVD (RPE-CVD)** – CVD process similar to PECVD except that the wafer substrate is not directly in the plasma discharge region. Removing the wafer from the plasma region allows processing temperatures down to room temperature. **Atomic layer CVD (AL-CVD)** – Deposits successive layers of different substances to produce layered crystalline films. **Hot wire CVD (HW-CVD)** – Also known as Catalytic CVD or hot filament CVD (HWCVD) uses a hot filament to chemically decompose the source gases. **Metalorganic chemical vapour deposition (MO-CVD)** – CVD process based on metalorganic precursors. **Hybrid physical chemical vapour deposition (HP-CVD)** – Vapour deposition process, that involve chemical decomposition of precursor gas and vapourization of a solid source. **Rapid thermal CVD (RT-CVD)** – CVD process that uses heating lamps or other methods to rapidly heat the wafer substrate. Heating only the substrate rather than the gas or chamber walls helps reduce unwanted gas phase reactions that can lead to particle formation.

1.3.2 **The process of chemical vapour deposition**

CVD processes are extremely complex and involve a series of gas phase and surface reactions. The basic steps in an overall CVD reaction are shown in Figure 1-6.

Step 1: Evaporation and transport of reagents (precursors) in the bulk gas flow region into the reactor

Step 2: Gas phase reactions of precursors in the reaction zone to produce Intermediates

Step 3: Mass transport of reactants to the substrate surface

Step 4: Nucleation and surface chemical reactions leading to film formation
Step 5: Mass transport of remaining fragments of the decomposition away from the reaction zone.

Figure 1-6: Process of chemical vapour deposition.

1.3.3 Precursors for CVD

1.3.3.1 Precursor requirements for CVD

Following are the general requirements for the precursors for CVD of thin film materials.

**Precursor purity:** It is desirable to have precursors with high level of purity to prevent contamination of the thin film with undesirable side products.

**Precursor reactivity:** The precursor needs to react at the substrate surface to give the desired thin film. Substrate surfaces are generally heated to a temperature of several hundred °C. The precursor should be reactive at these temperatures. However, one potential problem is that the precursor can react in the vapour phase throughout the reactor, as opposed to reacting only on the substrate surface. In general such reactions should be minimized to stop the resulting decomposition of the precursor in the reaction chamber.

**Volatility:** Volatility is a prerequisite for conventional LP-CVD. A precursor should be readily volatile at temperatures well below that of its decomposition.
**Stability in air:** It is desirable for a potential precursor to be stable under normal storage conditions to avoid the need for specialist storage.

**Toxicity:** The precursor should have a low degree of toxicity, without the need for specialist storage and special procedures during thin film growth.

**Synthesis:** The synthesis should be easy and adaptable to larger scale production without major problems.

**Environment and cost:** As environmental issues are becoming more important, it is advisable that new precursors should be non-toxic and based on abundant earth metals so that the price of the CVD precursor must be as low as possible.

1.3.4. Conventional precursors for CVD

The conventional precursors for MOCVD are usually highly volatile and toxic compounds such as metal alkyls, phosphines, and hydrogen selenide. Typical precursors for MOCVD of semiconductor materials are list in Table 1-4.
Table 1-4: MOCVD of some compound semiconductors \(^{1c}\).

<table>
<thead>
<tr>
<th>Semiconductors</th>
<th>Precursors</th>
<th>Growth Temp. (° C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>Me(_3)Ga, AsH(_3)</td>
<td>600-750</td>
</tr>
<tr>
<td>AlGaAs</td>
<td>Me(_3)Al, Me(_3)Ga, AsH(_3)</td>
<td>650-800</td>
</tr>
<tr>
<td>GaP</td>
<td>Me(_3)Ga, PH(_3)</td>
<td>700-800</td>
</tr>
<tr>
<td>Ga(AsP)</td>
<td>Me(_3)Ga, AsH(_3), PH(_3)</td>
<td>700-725</td>
</tr>
<tr>
<td>GaSb</td>
<td>Et(_3)Ga, Me(_3)Sb</td>
<td>500-550</td>
</tr>
<tr>
<td>AlAs</td>
<td>Me(_3)Al, AsH(_3)</td>
<td>700</td>
</tr>
<tr>
<td>GaN</td>
<td>Me(_3)Ga, NH(_3)</td>
<td>925-975</td>
</tr>
<tr>
<td>AlN</td>
<td>Me(_3)Al, NH(_3)</td>
<td>1250</td>
</tr>
<tr>
<td>InP</td>
<td>Me(_3)In, PH(_3)</td>
<td>650</td>
</tr>
<tr>
<td>InGaAs</td>
<td>Me(_3)In, Me(_3)Ga, AsH(_3)</td>
<td>650</td>
</tr>
<tr>
<td>InGaAlP</td>
<td>Me(_3)In, Me(_3)Ga, Me(_3)Al, PH(_3)</td>
<td>750</td>
</tr>
<tr>
<td>InSb</td>
<td>Me(_3)In, Me(_3)Sb</td>
<td>470</td>
</tr>
<tr>
<td>AlSb</td>
<td>Me(_3)Al, Me(_3)Sb</td>
<td>450</td>
</tr>
<tr>
<td>AlGaSb</td>
<td>Me(_3)Al, Me(_3)Ga, Me(_3)Sb</td>
<td>450</td>
</tr>
<tr>
<td>ZnS</td>
<td>Me(_2)Zn, H(_2)S</td>
<td>250-350</td>
</tr>
<tr>
<td>ZnSSe</td>
<td>Me(_2)Zn, H(_2)S, H(_2)Se</td>
<td>250-350</td>
</tr>
<tr>
<td>CdS</td>
<td>Me(_2)Cd, H(_2)S</td>
<td>300-400</td>
</tr>
<tr>
<td>CdSe</td>
<td>Me(_2)Cd, H(_2)Se</td>
<td>300-400</td>
</tr>
<tr>
<td>CdTe</td>
<td>Me(_2)Cd, (^{1})Pr(_2)Te</td>
<td>350-400</td>
</tr>
<tr>
<td>CdHgTe</td>
<td>Me(_2)Cd, Hg, (^{1})Pr(_2)Te</td>
<td>350-400</td>
</tr>
<tr>
<td>GaAs</td>
<td>Me(_3)Ga, AsH(_3)</td>
<td>600-750</td>
</tr>
</tbody>
</table>

The conventional multiple source MOCVD processes have many disadvantages such as (a) difficulty to control stoichiometry and (b) impurity incorporation, (c) unwanted side reactions and (d) high processing temperature which may cause inter-diffusion of layers. In order to overcome these disadvantages, during the past decades, much attention has been paid to the development of the alternative single-source precursors.

### 1.3.4 Advantages of the single source precursors

A single source precursor is a metal-organic molecule which contains all the desired elements for the growth of a compound material. The use of such molecular
precursor reagents may provide significantly improved processes for the fabrication of films due to the inherent control of the stoichiometry, fewer toxic precursors, and simplified fabrication compared to multiple-source processes. In addition, such precursors usually allow deposition of the desired phase at temperatures lower than those of the conventional multiple source processes. The uses of single source precursors for the CVD process have advantages over the conventional precursors which are:

- Control of the coordination numbers at the metal by the formation of adducts or aggregates can decrease the sensitivity towards the air and moisture
- Use of single source precursors can minimise the exclusion of toxic gases
- Prereactions may be limited
- Easy to maintain the stoichiometries of metal and ligand compositions
- The decomposition temperature is also controllable by design of the precursor consequently film growth at low temperature can be achieved
- It may also overcome the problem of incompatibility between the different precursors occasionally found in the conventional multiple source methods

1.4 Single source precursors for metal chalcogenide thin films

1.4.1 Precursors for II-VI semiconductor materials

The use of chemical routes for the deposition of semiconducting materials is not new but the growth of 11-VI films only became practical with Manasevit's use of volatile metal alkyls such as dimethylcadmium (Me\(_2\)Cd) and dimethylzinc (Me\(_2\)Zn) in a two-component mixture with H\(_2\)S, H\(_2\)Se, or Me\(_2\)Te using hydrogen as the carrier gas. A series of films including ZnS, ZnSe, CdS, CdSe, and CdTe were grown using this method but soon it was realized that a gas-phase reaction between metal alkyl and the chalcogenide took place in the mixing chamber with intermediates “(CH\(_3\)M(SH))” to less volatile oligomers, which nucleate crystal growth before reaching the substrate. This can result in the deposition of polycrystalline material of
non-uniform morphology. To overcome these limitations the following strategies were employed.

**The use of alternative chalcogenide precursors:** Alkyl chalcogenides can be used as alternative chalcogen sources. The chemistry of alkyl chalcogenide precursors have been described in several reviews. $^{3-7}$ MeSeH $^8$ Et$_2$Se $^9,10$ tBuSeH $^{11}$, tBu$_2$Se$^{12}$ have been used but lead to a need for higher deposition temperatures due to their thermal stability.

1.4.1.1 **Metal alkyl adducts**

Adducts of Zinc and cadmium alkyls with dioxan,$^{13-15}$ thioxan,$^{15}$ triethylamine $^{16-21}$ or triazine$^{16}$ have been used as precursors in MOCVD and can successfully inhibit pre-reaction of the chalcogenide and metal alkyls.$^{22,23}$ Adducts as precursors have several advantages including: (1) The vapour pressure of the metal alkyl is reduced in the adduct e.g. eliminating the necessity to cool bubblers containing dimethylzinc. (2) The chances of a homogeneous prereaction are considerably reduced (3) An improved quality of films due to the purification of the alkyl moiety during the preparation of the adduct.

1.5 **Single Source Precursors**

1.5.1 **Chalcogenolates as precursors**

The group 12 metal chalcogenolates are generally non-volatile and polymeric. These complexes are promising in several aspects: they can deliver both the metal and chalcogenide element in a defined ratio, avoiding any mixing problems or pre-reactions.

Figure 1-7: Structures of [MeZn(S'Bu)(Py)]$_2$ and [MeZn(S'Bu)]$_5$
These complexes have oligomeric structures such as of alkylzinc thiolates \([RZn(SR')]_n\): \([\text{MeZn}(S^{'Bu})]_5\) is a pentamer,\(^{24,25}\) \([\text{MeZn}(S^{'Pr})]_8\) is an octamer and \([\text{EtZn}(SEt)]_{10}\) is a decamer with a wurtzite-like cluster frame work\(^{26}\) (Figure 1-7).

Bochmann and co-workers\(^{27,28}\) have developed a range of precursors based on 2,4,6-tri-tert-butylphenylchalcogenolate for the deposition of II –VI materials. The single crystal structure of \([\text{Cd}(\text{SC}_6\text{H}_3^{'Bu}-2,4,6)]_2\) showed that the complex is a dimer. Polycrystalline CdS thin films were deposited at 450 °C by low pressure MOCVD using \([\text{Cd}(\text{SC}_6\text{H}_3^{'Bu}-2,4,6)]_2\) as precursor. During the deposition diarylsulfide was detected as a residual pyrolysate. The mercury analogues readily decomposed via a reductive elimination path to from atomic Hg and diaryl chalcogenide, which indicates that these compounds may be more suited for photo-assisted rather than thermal MOCVD method.\(^{29}\) The general preparation method of one such complex is shown in scheme 1.1, 1.2 and 1.3, of Figure 1-8.

Figure 1-8: A general preparation method of a complex.
1.5.2 Chalcogeno-ureato complexes as precursors

Cadmium sulfide films were grown by spray pyrolysis using aqueous mixtures of cadmium chloride and thiourea. The single molecule precursor was formed by reacting the parent compounds directly in the spray solution. Depending upon the pH, molar ratio and whether anhydrous or hydrated cadmium chloride was used, [Cd(SC(NH$_2$)$_2$)$_2$]Cl$_2$, [Cd(SC(NH$_2$)$_2$)$_2$]Cl$_2$, and [Cd(H$_2$O)(SC(NH$_2$)$_2$)]Cl$_2$ intermediates claimed. Niinisto et. al. have confirmed the formation of [Cd(SC(NH$_2$)$_2$)$_2$]Cl$_2$, a terahedrally coordinated cadmium complex with a quite complex thermal behaviour in air and under the conditions of spray pyrolysis, from which they concluded that it is not possible to produce CdS thin films without significant amounts of chlorine and other impurities. Similar results have also been obtained for the preparation of CdSe thin films using cadmium chloride and N,N-di-methylselonourea.

1.5.3 Dialkyldichalcogenocarbamato complexes as precursors

Dialkyldichalcogenocarbamates complexes of group 12 metals have been extensively used for the preparation of II-VI thin films by MOCVD. It is well known that the solid state pyrolysis of dithiocarbamate complexes under inert atmosphere generally give the corresponding metal sulfide. However, the stoichiometry and phase of the metal sulfide deposited are strongly dependent on the pyrolysis condition. Their general formula are [M(E$_2$CNR)$_2$] or [M(E$_2$CNR$^1$R$^2$)$_2$], according to whether they symmetrically or asymmetrically substituted. Single crystal structure determinations of various dialkyldichalcogenocarbamates, either symmetrically as [Zn(S$_2$CNMe)$_2$] with R = Me, Et, or Pr, and in [Cd(S$_2$CNMe)$_2$]$_2$, [Zn(Se$_2$CNEt)$_2$]$_2$ or unsymmetrically substituted as in [Zn(S$_2$CNMeR)$_2$]$_2$ with R = Et, Pr, or Bu, have shown dimeric associations [M(E$_2$CNR)$_2$]$_2$ with E = S, Se; M = Zn, Cd) in the solid state but are apparently monomeric in the vapour phase, as confirmed by mass spectra. Saunders et. al. pioneer to use diethyldithiocarbamate complexes of Zn and Cd as single source precursor for the deposition of ZnS, CdS by low-pressure MOCVD.
O’Brien et al.\textsuperscript{41} studied the deposition behaviour of the zinc complexes of unsymmetrically substituted dithiocarbamato ligands. In trial volatilization experiments they have shown that at \textit{ca} 150 °C, unsymmetrically substituted [Zn(S\textsubscript{2}CN(Me)Et)]\textsubscript{2}, [Zn(S\textsubscript{2}CN(Me)\textsuperscript{6}Pr)]\textsubscript{2} and [Zn(S\textsubscript{2}CN(Me)\textsuperscript{6}Bu)]\textsubscript{2} sublime above their melting points, whereas [Zn(S\textsubscript{2}CNEt\textsubscript{2})\textsubscript{2}] sublime as a solid. [Zn(S\textsubscript{2}CN(Me)\textsuperscript{6}Bu)]\textsubscript{2} was used successfully to grow ZnS on glass, in a cold wall, low-pressure MOCVD reactor, with the source at 150 °C and with a substrate temperature range of 450-490 °C. A film of hexagonal phase with a high degree of preferred (001) orientation was obtained in a 2h run at 470 °C. Similar comparative study of [Cd(SCN\textsubscript{2}Me\textsubscript{2})\textsubscript{2}] and [Cd(SCN(Me)\textsuperscript{6}Bu)\textsubscript{2}] has established the latter to be by far the more volatile.\textsuperscript{42}

1.5.4 \textbf{Mixed alkyl/dialkyldichalcogenocarbamato complexes as precursors}

The volatility of dichalcogenocarbamate complexes has been increased by making associates of alkyl ligand, so as to form heteroleptic complexes of general formula [M(R)(E\textsubscript{2}CNR’\textsubscript{2})]. (Me)Zn(diethylthiocarbamate)\textsuperscript{43} and (Me)Zn(dialkyldiselenocarbamate)\textsuperscript{44} have been shown to be dimers, with [EZn(\mu-E)]\textsubscript{2} cores, in the solid state. These compounds were first prepared by Nolte\textsuperscript{45} using the insertion reactions (1.4) and (1.5).

\begin{align*}
2 \text{MeZn(NEt}_{2}) + 2\text{CS}_2 & \rightarrow \text{[MeZn(S}_2\text{CNEt}_{2})\text{]_2} \quad (1.4) \\
\text{Me}_{2}\text{Zn} + \text{Zn(S}_2\text{CNEt}_{2})\text{]_2} & \rightarrow \text{[MeZn(S}_2\text{CNEt}_{2})\text{]_2} \quad (1.5)
\end{align*}
Conproportionation also provides a convenient synthesis for these compounds.

Complexes with general formula \([M(R)(E_{2}CNR^{'2})]\) (R or R’=Me or Et, M=Zn; R=Me, R’=Et, M=Cd) have been shown to sublime under mild conditions (100-50°C). Films of ZnS, ZnSe, CdSe and Zn_{0.5}Cd_{0.5}Se have been grown by LP-MOCVD on glass plates at 450 °C from \([((R)Zn(S_{2}CNEt_{2}))_{2}]\) with (R = Me,^{43} Me_{3}C and Me_{3}CCH_{2}),^{46} [(Me)Cd(Se_{2}CNEt_{2})]_{2} and [(Me)Zn_{0.5}Cd_{0.5}(Se_{2}CNEt_{2})]_{2} in a hot wall reactor.

1.5.5 Xanthatometal complexes as precursors

Nanocrystalline ZnS and CdS thin films were deposited onto SiO_{2} substrates by CVD at temperatures between 200 °C and 450 °C from \([M(C_{3}H_{7}OCS_{2})_{2}]\) (M=Zn,Cd) as single-source precursors.^{47} Thermal decomposition and fragmentation of \([M(C_{3}H_{7}OCS_{2})_{2}]\) was also investigated by thermal analyses and mass spectrometry.

Barrecal et.al. investigated the properties of \(M(S_{2}COCHR)_{2}\), M=Cd and R=ethyl or isopropyl) as potential single-source molecular precursors for the chemical vapour deposition (CVD) of CdS thin films.^{48}

![Figure 1-10: Structure of \([Cd(C_{3}H_{7}OS_{2})_{2}]_{n}\) (Omitted).](image)

The structure of bis(O-isopropylthio-carbonato)cadmium(II) \([Cd(C_{3}H_{7}OS_{2})_{2}]\) is shown in Figure 1-10.^{49} Two distinct motifs are known for \([Cd(S_{2}COR)_{2}]\), a square-
planar geometry with \( R = \text{CH}_2\text{CH}_2\text{OMe} \), and weak Cd-S interactions above and below the square plane\(^{50}\) and tetrahedrally coordinated Cd, i.e. when \( R = \text{Et} \)\(^{51}\) and \( R = \text{Bu} \)\(^{52}\).

The recently reported structure of \([\text{Cd}(S_2\text{COC}_3\text{H}_7)_2]\) also conforms to this motif.\(^{53}\)

1.5.6 Monothiocarbamato complexes as precursors

Bis(diethylmonothiocarbamato)cadmium(II) have shown reasonable volatility, despite the polymeric structure\(^{54}\) and was used to deposit films of CdS by LP-MOCVD at temperatures between 300-400 °C.\(^{55}\) Compounds with the general formulæ \( \text{M}(\text{SOCR})_2(\text{tmeda}) \) (tmeda =N,N,N,N-tetramethylethylenediamine, \( R = \text{methyl} \)\(^{56}\) or tert-butyl\(^{57}\) were used to grow CdS, ZnS, and \( \text{Cd}_x\text{Zn}_{1-x}\text{S} \) by AACVD method. \( \text{Zn}(\text{SOCCH}_3)_2(\text{tmeda}) \) and \( \text{Cd}(\text{SOCCH}_3)_2(\text{tmeda}) \) are isostructural, monomeric complexes in the solid state, with the metal atom in a distorted tetrahedral coordination environment comprising two nitrogens and two sulphurs.\(^{56}\)

1.5.7 Dichalcogenophosphinatometal complexes as precursors

Chalcogenophosphinates are another class of compounds which have been studied as single source precursors for the deposition of II-IV thin materials. CdS thin films were grown using dimethylthiophosphinates found that doping of excess phosphorus on n-type CdS films would lead to highly compensated semi insulating material.\(^{58}\) Thin films of ZnS and CdS were grown from \([\text{M}(\text{S}_2\text{P}^\prime\text{Bu}_2)_2]\) (M=Zn, Cd) using homemade cold-wall low-pressure reactor.\(^{59}\) O’Brien et. al.\(^{60,61}\) recently reported a series of metal complexes of selenophosphinates with the general formula \([\text{M}(\text{R}_2\text{PSe}_2)_n]\) (M = Zn, Cd, Pb, In, Ga, Cu, Bi, Ni; \( R = \text{t}^\prime\text{Pr, Ph} \)) for the deposition of metal selenide thin films.

1.5.8 Dichalcogenoiminophosphinatometal complexes as precursors

Cadmium complex of diselenodiisopropyliminophosphinates were prepared by Woolins et. al. from diisopropylphosphine via a two step strategy as shown in Equation 1-1-Equation 1-3. The \( \text{NH}(\text{SeP}^\text{iPr}_2)_2 \) ligand is more thermally stable than bulky selenolate lignads, such as \([\text{SeSi}(\text{SiMe}_3)_3]\), and thermolysis of its complexes produces cleaner products with reduced contamination which makes them suitable precursors for the deposition of CdSe thin films.\(^{62}\) The complex \([\text{MeCd}(\text{SeP}^\text{Pr}_2)_2\text{N}_2]\) was prepared by conproportionation of \( \text{Me}_2\text{Cd} \) and \([\text{Cd}(\text{SeP}^\text{Pr}_2)_2\text{N}_2]\) in toluene (Figure 1-11). Single crystal structure of the complex showed the dimeric nature of
molecule; each diselenoimidodiohosphinate relates to one cadmium atom and bridges to next, with each cadmium is four coordinates and bound to three selenium atoms and one carbon.  

\[ \text{Equation 1-1:} \quad \text{NH(SiMe}_3\text{)}_2 + \text{iPr}_2\text{PCl} \xrightarrow{\text{E = S, Se}} \text{NH(P}^{\text{iPr}}\text{Pr}_2\text{)}_2 + 2\text{ClSiMe}_3 \]

\[ \text{Equation 1-2} \quad \text{NH(P}^{\text{iPr}}\text{Pr}_2\text{)}_2 \xrightarrow{\text{NaOMe, MeOH}} \text{NH(EP}^{\text{iPr}}\text{Pr}_2\text{)}_2 \]

\[ \text{Equation 1-3} \quad 2\text{NH(EP}^{\text{iPr}}\text{Pr}_2\text{)}_2 \xrightarrow{\text{MeOH}} \text{M([EP}^{\text{iPr}}\text{Pr}_2\text{)}_2\text{N]}_2 + 2\text{NaCl} \]

Figure 1-11: Structure of Cd[N(SeP}^{\text{iPr}}\text{Pr}_2\text{)]_2.

1.5.9 Dimorpholinodithioacetylacetonatometal complexes as precursors

The ligand dimorpholinodithioacetylacetonate (msacmsac) was prepared by the reaction of morpholine with sulphur and allyl propylether at 110 °C for several hours. Subsequent reaction of the ligand with cadmium nitrate resulted in corresponding complex. The structure of the complex is shown in Figure 1-12. CdS thin films comprising of nanorods were obtained by AACVD method.

1.5.10 Thiobiurets and dithiobiurets

Thiobiurets and dithiobiurets have only recently been explored for the synthesis of metal complexes and deposition of materials including with Co, Ni, Fe, Zn, Cd, In, Cu. Although thiobiuret, dithiobiurets and their related compounds has attracted a
considerable attention due to their physiological and potential chemotherapeutic properties, and their possible technical applications in the field of plastics and resins. Armstrong et al. described the synthesis of Zn complex of 1,1,5,5-tetraethyl-2-thiobiuret.

The reaction of N,N'-dialkylcarbamyl chloride, sodium thiocyanate and dialkylamine produced 1,1,5,5-tetraalkyl-1-2-thiobiuret ligand in high yield. Addition of methanolic solution of metal acetate to this reaction gave corresponding metal complexes. The same method was followed to prepare dithiobiuret complexes starting with N,N'-dialkylthiocarbamyl chloride. The structure of zinc complex [Zn(S$_2$N$_3$C$_{10}$H$_{20}$)$_2$] (Figure 1-13) shows that it has distorted tetrahedral geometry with the ligand bite angles of 102.55(2)$^\circ$ and 103.41(2)$^\circ$ somewhat smaller than the perfect tetrahedral angle. All of these complexes have been used as (SSP) Single Source Precursor to deposit thin films of metal chalcogenides by AACVD.

Figure 1-12: Structure of ligand msacmsac and cadmium complex [Cd(msacmsac)(NO$_3$)$_2$].
1.6 Precursors for III-VI semiconductor materials

1.6.1 Dichalcogenocarbamatometal complexes as precursors

O’Brien and co-workers explored the precursor chemistry of chalcogenocarbamato complexes to deposit III-VI materials. Indium sulfide thin films were grown from dimethyl-, diethyl- or dineopentyl-indium diethylidithiocarbamates [R₂In(S₂CNEt₂)] with (R = Me, Et, or Np) on GaAs substrate, using a cold wall low-pressure reactor. The phases deposited from Me₂InS₃CNEt₂ were either β-In₂S₃ at 325 °C, In₆S₇ at 350 °C and 375 °C or InS + In₆S₇ at 400 °C and 425 °C. [Et₂In(S₂CNEt₂)] yielded β-In₂S₃ at 350 °C and 400 °C, whereas [Np₂In(S₂CNEt₂)] gave In₆S₇ at 375 and 400 °C. The ethyl complex differs from the other two, both by its aptitude for β-H elimination, and the production of single phase cubic β-In₂S₃ over entire temperature range studied.

The analogous gallium precursors proved less effective to produce gallium sulfide thin films. Unsymmetrically substituted indium tris-chelate complexes of dichalcogenocarbamate [In(E₂CN(Me)R)₃] were E = S or Se, R = n-butyl or n-hexyl have been used as precursors for the deposition of In₂S₃ on glass, (100)-GaAs or (111)-InP using cold wall reactor under low pressure at 450-500 °C. Similarly mixtures of cubic and hexagonal In₂Se₃ films were produced from the methylhexyldiselenocarbamate of indium complex.

Figure 1-13: Structure of Zn[N(SCNEt₂)₂]. Alkyl groups are removed for clarity.
1.6.2 Xanthatometal and monothiocarboxylatometal complexes as precursors

Highly (111) direction oriented cubic α-In$_2$S$_3$ films were grown on glass using [In(S$_2$COiPr)$_3$] at 210 °C. Hampden-Smith and co-workers have taken the facile elimination of thioacetic anhydride from polyether adducts of group 2 metal thioacetates and applied it to adducts of gallium and indium thioacetates. Two gallium complexes, [Ga(SCOMe)$_2$(CH$_3$)(dmp)] and [Ga(SCOMe)$_3$(dmp)] (dmp = 3,5-dimethylpyridine) and an ionic complex, [Hdmp][In(SCOCH$_3$)$_4$] have been employed in aerosol-assisted MOCVD experiments to prepare thin films of the metal sesquisulfides.

1.6.3 Metal complexes of chalcogenophosphinates and iminochalcogenophosphinates as precursors

Diselenophosphinates of indium and gallium complexes have been prepared by O’Brien and co-workers and used as single source precursors for the deposition of indium selenide, gallium selenide by aerosol assisted chemical vapour deposition. The single crystal structure of indium complex shows the expected tris chelate octahedral geometry. All three diselenophosphate ligands are chelating to form three 4-membered rings (Se-P-Se-In) with In-Se bond distances of 2.729(6)-2.768(6) Å. In contrast, gallium complex [Ga(iPr$_2$PSe$_2$)$_3$] is four-coordinate around gallium. The structure consists of one chelating and two pendant diisopropylidiselenophosphinate ligands in a distorted tetragonal geometry (Figure 1-14).

Similarly thin films of hexagonal In$_2$Se$_3$ and cubic Ga$_2$Se$_3$ were deposited by AACVD and LPCVD using dialkyldiselenoiminophosphinates of indium or gallium [R$_2$M(SePPr$_2$)$_2$N] (M = In or Ga; R = Me, Et) as single source precursors. [M(µ-Te)(N(iPr$_2$PTE)$_2$)$_3$] (M = In, Ga) have been employed to deposit M$_2$Te$_3$ films onto glass and Si(100) substrate at 325-475 °C. The indium complex gave cubic In$_2$Te$_3$ exclusively, whereas the gallium complex yielded mixtures of cubic Ga$_2$Te$_3$, monoclinic GaTe and hexagonal Te.
1.7 Precursors for transition metal chalcogenide materials

Cheon et. al.\textsuperscript{79} have reported the deposition of NiS by both a thermal and photochemical CVD using [Ni(S\textsubscript{2}COCHMe)\textsubscript{2}]. Recently O’Brien et. al.\textsuperscript{80} deposited NiS thin films on glass by aerosol assisted chemical vapour deposition (AACVD) using single source precursors of the type, ([Ni(S\textsubscript{2}COR)\textsubscript{2}], R = C\textsubscript{2}H\textsubscript{5} or C\textsubscript{3}H\textsubscript{7}). The metal alkyl xanthate compounds, M(S\textsubscript{2}COCHR)\textsubscript{2}, M = Ni and R = ethyl or isopropyl were prepared by stoichiometric reaction of potassium alkyl xanthate and metal salts following the literature method\textsuperscript{81-83} which involved the reaction of an aqueous solution of the corresponding metal salt with the potassium xanthate aqueous solution.

TiS\textsubscript{2} and MoS\textsubscript{2} thin films were deposited using [M(S\textsubscript{t}Bu)\textsubscript{4}] as the precursor through conventional hot wall LP-MOCVD. The precursor was heated to 45 °C and the substrate in the range 150-270 °C for TiS\textsubscript{2} and 110-350 °C for MoS\textsubscript{2} using adducts of titanium tetrachloride with cycloalkanethiols and alkylselenium.\textsuperscript{84} Volatile phosphinochalcogenoic amidato complexes of general formulae [M(‘Bu\textsubscript{2}P(E)NR\textsubscript{2})\textsubscript{2}] with E = Se, Te, have been prepared for 3-d transition metal elements from chromium to nickel.\textsuperscript{85} Thermolysis studies under hot wall LP-MOCVD conditions have resulted in the growth of several metal chalcogenides thin films on glass substrate at 300-400 °C. Thin films of nickel sulfide and palladium sulfide have been prepared from metal complexes of bis(isopropylxanthate) [M(S\textsubscript{2}COCHMe\textsubscript{2})\textsubscript{2}] (M = Ni or Pd).\textsuperscript{86} The
precursors were sublimed at 95 °C (Ni) and 110 °C (Pd) under 10⁻² torr and depositions occurred on glass or silicon wafers at 300 °C for NiS and 350 °C for PdS. Nomura et al. have grown copper-deficient Cu₁.₉₆S films by LP-MOCVD from copper(II) bis(diethyl-dithiocarbamate, [Cu(S₂CNEt₂)₂] using N₂ as carrier gas with source temperature of 200 °C and deposition temperature of 400 °C on silica substrate. The same precursor has been employed in RPECVD experiments to grow Cu₂S films at the deposition temperature range of 200-400 °C under helium. O’Brien and co-workers have deposited high-purity Cu₂S and Cu₂Se thin films from the [Cu(E₂CN(Me)Hex)₂] (E = S or Se) precursors respectively. Pyrite FeS₂ thin films have been deposited using symmetrical and unsymmetrical dialkyl dithiocarbamate complexes of iron [Fe(S₂CNRR')₃] R = Me, 'Bu; R' = 'Pr, "Bu by AACVD in the temperature range of 375-450 °C. Cubic manganese sulfide thin films were deposited from [Mn(S₂CN(Me)Hex)₃] on glass substrate under argon flow rate of 200 ccm at the temperature range of 475-500 °C. Similarly thin films of cobalt sulfides were deposited from cobalt complex of methylhexyldithiocarbamate in the temperature range of 375-475 °C on glass substrate by AACVD and obtained mixture of Co₁ₓS, CoS₂ and Co₃S₄. O’Brien et al. achieved deposition of nickel selenide and nickel phosphide thin films using imido-bis-(diisopropylthioselenophosphinate) of nickel(II), [Ni(Pr₂P(S)NP(Se)Pr₂)₂], complex (Figure 1-15) in the temperature range of 375-475 °C by cold wall LP-MOCVD on glass. Nickel phosphide films were deposited in the temperatures between 475 and 425 °C. Nickel selenide films were deposited in the temperature between 375 and 400 °C.
1.8 Scope of the present study

The aim of the present study is to synthesize a series of different metal (Zn, Cd, Cu, Ag, Ni, Co, In, Ga etc) complexes with rarely used N-methyl-N,N-dimethylethylene/-propylenediaminodithiocarbamato ligands. The synthesized complexes will then be characterized by microelemental analysis, NMR and X-ray crystallography. Fully characterized complexes will then be used as single source precursors to deposit binary and ternary metal sulfide thin films by AACVD method.
1.9 References


76. C. Q. Nguyen, M. Afzaal, M. A. Malik, P. O’Brien, unpublished result


Chapter 2: AACVD

Deposition of ZnS and CdS Thin Films From

\[ [M(S_2CN(Me)(CH_2)_nN(Me)e)_2]_2 \] (M = Zn or Cd; n = 2 or 3).

Chapter 2 consists of two major sections. Section 1 consists of ZnS and the section 2 on CdS. It starts with a brief background of each semiconductor material and the methods or precursors used for its deposition by AACVD. The X-ray structures of newly synthesised compounds \( N,N\)-Dimethylimidazolidine-2-thione (1), \( M(S_2CN(Me)(CH_2)_nN(Me)e)_2 \) (M = Zn, Cd; n = 2 or 3) (2), (3), (4) and (5) have been determined and then their use as single source precursors to deposit ZnS and CdS thin films onto glass substrates by AACVD is described.
2.1 Zinc sulfide

Zinc sulfide is a white to yellow-coloured solid. It is found in two forms, the more stable cubic form, known also as zinc blend or sphalerite and the hexagonal or wurtzite form. In the bulk state, ZnS typically exists as the zinc blende (cubic) form at room temperature. At elevated temperatures, bulk ZnS can undergo a phase transformation from the cubic structure to the hexagonal wurtzitic form. The hexagonal form has more desirable optical properties than the cubic form. A tetragonal form is also known as very rare mineral polhemusite (Zn,Hg)S. Both sphalerite and wurtzite are intrinsic wide-bandgap semiconductors. The cubic form has a band gap of 3.54 eV whereas the hexagonal form has a band gap of 3.91 eV.

Zinc sulfide, with addition of few parts per million of suitable activator, is used as phosphor in many applications, from cathode ray tubes through X-ray screens to glow in the dark products. When silver is used as activator, the resulting colour is bright blue, with maximum at 450 nm. Manganese yields an orange-red colour at around 590 nm. Copper provides long glow time and the familiar glow-in-the-dark greenish colour. Copper doped zinc sulfide is used also in electroluminescent panels. It can be doped as both n-type semiconductor and p-type semiconductor.

Zinc sulfide is a direct wide band gap semiconductor with a high index of refraction and good transmittance in the visible range. It is one of the most important materials in photonics research. When it is doped with elements such as Eu and Tb, a wide range of exciting optical properties can be evolved.

2.1.1 Zinc sulfide thin films

The deposition of thin films from the gas phase can be carried out by many different methods mainly belonging to two families: physical and chemical vapor deposition (PVD, CVD). Both methods use physical transport of the vapor species to the deposition site. Deposition techniques belonging to PVD family such as evaporation or sputtering processes have been used for the growth of ZnE (E = S, Se, Te) and ZnO thin films. The deposition of ZnE (E = S, Se, Te) thin films by CVD techniques has been widely studied. The first reports of ZnS by MOCVD used diethylzinc (Et₂Zn) in the presence of hydrogen sulfide (H₂S). Although good
quality thin films of, for example, ZnSe with excellent electrical and optical properties have been obtained, at low substrate temperature (~ 300 °C) a severe premature reaction frequently occurs in the gas phase. The premature reaction during ZnS or ZnSe growth can be attributed to the facile elimination of alkyl groups from R₂Zn by acidic hydrogen from H₂Se or H₂S. Much effort has therefore gone into developing alternative precursors which are less likely to undergo such parasitic reactions.

One alternative approach has been to modify the zinc precursor so that it will be less volatile. For instance, the adducts [Me₂Zn(1,4-dioxane)] and [Me₂Zn(1,4-thioxane)] have been shown to reduce pre-reaction with H₂Se, while still allowing the growth of ZnSe at low temperature (200-350 °C). A significant advance was achieved by the use of a nitrogen donor adduct, dimethylzinc triethylamine [(Me₂Zn)(NEt₃)], as a precursor for ZnS or ZnSe. There are a number of significant advantages associated with its use. Firstly, the premature reaction with H₂Se or H₂S is eliminated rather than merely inhibited. Secondly, [(Me₂Zn)(NEt₃)] is not pyrophoric and is less susceptible to contamination by oxygen containing impurities (e.g., (MeO)ZnMe). [(Me₂Zn)(NEt₃)] is also much easier to purify than Me₂Zn. Finally, it has been shown that [(Me₂Zn)(NEt₃)] forms a eutectic mixture, leading to a more reproducible delivery of the precursor.

Thiolato and the other chalcogenolato complexes of zinc and cadmium are the simplest candidates as single-source precursors of zinc or cadmium chalcogenides. Bochmann et al. have extended such chemistry by synthesizing a range of precursors based on 2,4,6-tri-tert-butylphenylchalcogenolates, and these have been used to deposit thin films of the metal sulfides and selenides in preliminary low-pressure growth experiments. Other single source precursors used to deposit a range of chalcogenides include M[ESi(SiMe)₃]₂ (M = Zn, Cd, Hg; E = S, Se or Te) synthesised by Arnold et al.

Thiophosphinato complexes are yet another class of chalcogen containing compounds that may be useful as precursors. Takahashi et. al. deposited cadmium and zinc sulfides using methylthiophosphinates [M(S₂PMe₂)₂] (M = Cd, Zn). Dithiocarbamato complexes are another potential candidate as precursors for metal sulfide.
preparations, especially as their lower alkyl derivatives are generally crystalline solids but are significantly volatile. Wold and co-workers\textsuperscript{26} have studied the decomposition products of [Zn(S\textsubscript{2}CNEt\textsubscript{2})\textsubscript{2}] using GC-MS and reported the deposition pathway involves clean elimination of ZnS from the precursor. The decomposition of \textit{N,}\textit{N-}
dialkyldithiocarbamato complexes is believed to occur through a free radical decomposition route, which is consistent with the formation of disulfide products from the thermal decomposition of these complexes.\textsuperscript{28} It has also been noted that \textit{N,}\textit{N-}
dialkyldithiocarbamato complexes are more stable than their corresponding \textit{N-}
alkyldithiocarbamato complexes due to the lack of acidic hydrogen atoms at the nitrogen.\textsuperscript{29}

2.1.2 Synthesis and X-ray crystal structure of \textit{N,}\textit{N-}
Dimethylimidazolidine-2-thione (DMIT) (1) and [Zn(H\textsubscript{2}O)(S\textsubscript{2}CN(Me)(CH\textsubscript{2})\textsubscript{2}N(Me))\textsubscript{2}] (2)

White crystalline compound was crystallised from the reaction of \textit{N, N, N-}
trimethylethylenediamine with carbon disulfide in methanol at room temperature. The compound was identified as \textit{N, N-Dimethylimidazolidine-2-thione (DMIT) (1)} by elemental analysis (see experimental section for analytical). The crystal structure of this compound was determined by X-ray single crystallography. Crystal data and structure refinement for the ligand (1) is given in Table 2-1. Figure 2-1 shows the X-ray structure of \textit{N, N-dimethylimidazolidine-2-thione (DMIT) (1).}\textsuperscript{30} \textit{N,N'-}
dimethylimidazolidine-2-thione and 2,3-dihydro-1,2,5-trimethyl-1,2,4-triazole-3-thione have been used to measure the rate constants and activation enthalpies for the reaction with methyl iodide in acetonitrile-methanol mixtures. The structure of the compound (1) is very simple as predicted by other methods.\textsuperscript{30} C-S and C-N bond distances are as expected for a double and single bonds respectively. The S-C-N angles (108, 125°) give it a sp\textsuperscript{2} hybridization and close to planar shape.
Reaction mechanism for DMIT synthesis

\[
\begin{align*}
\text{Trimethylethenediamine} & \quad \xrightarrow{\text{NaOH/ MeOH, Ice bath}} \quad \text{DMIT}\:
\end{align*}
\]

Table 2-1: Crystal data and structure refinement for \( N,N \)-Dimethylimidazolidine-2-thione (DMIT) (1).

<table>
<thead>
<tr>
<th>Compound</th>
<th>( N,N )-Dimethylimidazolidine-2-thione (DMIT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>( \text{C}<em>5\text{H}</em>{10}\text{N}_2\text{S} )</td>
</tr>
<tr>
<td>Formula weight</td>
<td>130.21</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, ( \text{P2(1)/n} )</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>( a = 10.230(2) \text{ Å} \quad \alpha = 90^\circ \quad b = 5.9698(12) \text{ Å} \quad \beta = 112.456(4)^\circ \quad c = 11.503(2) \text{ Å} \quad \gamma = 90^\circ )</td>
</tr>
<tr>
<td>Volume</td>
<td>( 649.2(2) \text{ Å}^3 )</td>
</tr>
<tr>
<td>( Z ), Calculated density</td>
<td>4, ( 1.332 \text{ Mg/ m}^3 )</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.391 mm(^{-1} )</td>
</tr>
<tr>
<td>Crystal size</td>
<td>( 0.30 \times 0.20 \times 0.04 \text{ mm} )</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>( 2.27 ) to ( 28.23^\circ )</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>( 1515 / 0 / 75 )</td>
</tr>
<tr>
<td>Goodness-of-fit on ( F^2 )</td>
<td>0.816</td>
</tr>
<tr>
<td>Final ( R ) indices ([I&gt;2\sigma(I)])</td>
<td>( R_1 = 0.0382, \quad wR_2 = 0.0503 )</td>
</tr>
<tr>
<td>( R ) indices (all data)</td>
<td>( R_1 = 0.0680, \quad wR_2 = 0.0545 )</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>( 0.442 ) and ( -0.299 \text{ e.Å}^{-3} )</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>( 3936 / 1515 ) [( R \text{(int)} = 0.0561 )]</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>(-12 \leq h \leq 13, \quad -6 \leq k \leq 7, \quad -3 \leq l \leq 14 )</td>
</tr>
</tbody>
</table>
Important bond lengths (Å) and angles (°): C(1)-N(1) 1.343(2), C(1)-N(2) 1.355(2), C(1)-S(1) 1.680(2), C(2)-N(1) 1.454(2), N(1)-C(1)-N(2) 108.55(17), N(1)-C(1)-S(1) 125.82(15), N(2)-C(1)-S(1) 125.63(15), N(2)-C(3) 1.459(2), N(2)-C(5) 1.444(3), N(1)-C(4) 1.447(2), C(2)-C(3) 1.531(3).

2.1.2.1 X-ray structure of [Zn(H₂O)(S₂CN(Me)(CH₂)₂N(Me)₂)₂] (2)

Compound (2) was synthesised in situ by the reaction of N,N,N-trimethylethylene diamine with carbon disulfide and with zinc salt in methanol at room temperature (full details in experimental section). The complex was crystallised from hot toluene to give transparent plates which were used to determine the X-ray single crystal structure of this complex. This compound without the presence of oxygen has been reported by O’Brien group \(^{31}\) but several attempts to crystallise the compound for the determination of X-ray crystal structure were unsuccessful. The presence of water molecule in this structure may have been caused by the wet solvent in the reaction mixture.

Figure 2-1: Structure of N,N-Dimethylimidazolidine-2-thione (DMIT) (1).
The Crystal data and structure refinements of compound (2) are given in Table 2-2\textsuperscript{33-36}. The molecular structure of the complex is shown in Figure 2-2. The structure is based on a monomer unlike the structure of a related cadmium compound, \{MeCdS\textsubscript{2}CN(Me)(CH\textsubscript{2})\textsubscript{3}N(Me)\textsubscript{2}\}\textsubscript{n}, which is a polymer.\textsuperscript{32} The geometry around zinc atom is close to the square pyramidal. Zinc is coordinated by four sulphur atoms from two ligands (bidentate) and an oxygen atom. The S-Zn bond distance are close to those reported for a number of dithiocarbamato metal complexes by O’Brien group.\textsuperscript{33-36}
Table 2-2: Crystal data and structure refinement for 
\([\text{Zn(H}_2\text{O)}(\text{S}_2\text{CN(Me)(CH}_2)_2\text{N(Me)}_2)_2] \) (2)\textsuperscript{33-36}.

<table>
<thead>
<tr>
<th>Compound</th>
<th>[\text{Zn(H}_2\text{O)}(\text{S}_2\text{CN(Me)(CH}_2)_2\text{N(Me)}_2)_2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>\text{C}<em>{12}\text{H}</em>{28}\text{N}_4\text{OS}_4\text{Zn}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>437.99</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, \text{C}2/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>\begin{align*} a &amp;= 16.136(3) \text{ Å} &amp; \alpha &amp;= 90^\circ \ b &amp;= 8.6540(14) \text{ Å} &amp; \beta &amp;= 92.271(3)^\circ \ c &amp;= 14.344(2) \text{ Å} &amp; \gamma &amp;= 90^\circ \end{align*}</td>
</tr>
<tr>
<td>Volume</td>
<td>2001.5(6) \text{ Å}^3</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>4, 1.454 \text{ Mg/m}^3</td>
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<tr>
<td>Absorption coefficient</td>
<td>1.650 \text{ mm}^{-1}</td>
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<td>Crystal size</td>
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</tr>
<tr>
<td>Theta range for data collection</td>
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<td>Data / restraints / parameters</td>
<td>2001 / 0 / 108</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>1.055</td>
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<tr>
<td>Final R indices [(I&gt;2\sigma(I))]</td>
<td>(R_1 = 0.0366, \ wR_2 = 0.0867)</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>(R_1 = 0.0416, \ wR_2 = 0.0896)</td>
</tr>
<tr>
<td>Compound</td>
<td>((\text{H}_2\text{O}) \text{(S}_2\text{CN(Me)(CH}_2)_2\text{N(Me)}_2)_2)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.514 and -0.371 \text{ e.Å}^{-3}</td>
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<td>Reflections collected / unique</td>
<td>4050 / 2001 [R(int) = 0.0420]</td>
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<tr>
<td>Limiting indices</td>
<td>-19&lt;(h&lt;20, -3&lt;(k&lt;10, -17&lt;(l&lt;13)</td>
</tr>
</tbody>
</table>

Hogarth \textit{et al} \textsuperscript{37} prepared a number of similar \textit{bis} and \textit{tris}-dithiocarbamato complexes, \([\text{M}\{\text{S}_2\text{CN(\text{CH}_2})_3\text{NMe}_2\}_2]\) (\text{M} = \text{Cu}, \text{Ni}), \([\text{M}\{\text{S}_2\text{CN(\text{CH}_2})_3\text{NMMe}_2\}_2]\) (\text{M} = \text{Cu}, \text{Pd}) and \([\text{Co}\{\text{S}_2\text{CN(\text{CH}_2})_3\text{NMe}_2\}_2\}_3]\) and their structures were determined by X-ray crystallography. All four \textit{bis} metal-complexes adopt the square planar coordination geometry as expected. All were monomeric with no significant intermolecular interactions. The Zn-O distance was comparatively smaller (2.00 \text{ Å}) than those reported for \([\text{(Me}_2\text{NCH}_3)\text{Zn(O}_2\text{CNEt}_3}\] (Zn-O, 2.04-2.26 \text{ Å}).\textsuperscript{38}
Figure 2-2: Molecular structure of \([\text{Zn(H}_2\text{O})(\text{S}_2\text{CN(Me)(CH}_2)_2\text{N(Me)}_2)]\) (2).

Zn(1)-O(1) 2.000(2), Zn(1)-S(2) 2.3528(7), Zn(1)-S(1) 2.5726(7), S(1)-C(1) 1.713(2), S(2)-C(1) 1.730(2), O(1)-H(1O) 0.86(3), O(1)-Zn(1)-S(2) 112.771(18), O(1)-Zn(1)-S(1) 96.298(16), S(2)-Zn(1)-S(1) 73.46(2).

2.1.2.2 Synthesis and X-ray structure of \([\text{Zn(S}_2\text{CN(Me)(CH}_2)_3\text{N(Me)}_2)]\) (3)

The complex (3) was prepared by the reaction of \(N,N,N\)-trimethylpropylenediamine with carbon disulfide and then with zinc salt in methanol at room temperature (full details in experimental section). The complex was crystallized from toluene to give white cubic crystals which were used to determine the X-ray single crystal structure of the complex. The compound is air and moisture stable at room temperature for long periods of time.

The structure of (3) consists on \([\text{Zn(S}_2\text{CN(Me)(CH}_2)_3\text{N(Me)}_2)]\) units linked through metal and nitrogen atoms of dimethyl amino groups to form a polymer. Each zinc atom is coordinated by four sulphur atoms of dithiocarbamato groups and the nitrogen atom from the dimethylamino group of the next molecule forming intermolecular interactions (Zn-N, 2.11 Å). The crystal data and structure refinements of compound (3) are given in Table 2-3 and the structure is shown in Figure 2-3. All the bond lengths and angles are close to those observed for \([\text{Zn(H}_2\text{O})(\text{S}_2\text{CN(Me)(CH}_2)_2\text{N(Me)}_2)]\) (2) and also to those reported for other similar dithiocarbamato metal complexes.\(^{32-36}\)
Table 2-3: Crystal data and structure refinement $\text{Zn}(\text{S}_2\text{CN(Me)}(\text{CH}_2)_3\text{N(Me)}_2)_2$ (3).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$[\text{Zn}(\text{S}_2\text{CN(Me)}(\text{CH}_2)_3\text{N(Me)}_2)_2]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>$\text{C}<em>{14}\text{H}</em>{30}\text{N}_4\text{S}_4\text{Zn}$</td>
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<td>Crystal system, space group</td>
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<td>Unit cell dimensions</td>
<td>$a = 7.5187(8)$ Å, $\alpha = 90^\circ$, $b = 12.0632(12)$ Å, $\beta = 108.402(2)^\circ$, $c = 11.6744(12)$ Å, $\gamma = 90^\circ$</td>
</tr>
<tr>
<td>Volume</td>
<td>1004.72(18) Å$^3$</td>
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<td>Z, Calculated density</td>
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</tr>
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<td>$R1 = 0.0588$, $wR2 = 0.0996$</td>
</tr>
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<td>Largest diff. peak and hole</td>
<td>0.687 and -0.679 e.A$^{-3}$</td>
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<td>Reflections collected / unique</td>
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</tr>
<tr>
<td>Limiting indices</td>
<td>$-9 \leq h \leq 8$, $-16 \leq k \leq 15$, $-15 \leq l \leq 13$</td>
</tr>
</tbody>
</table>
Figure 2-3:  (a) Molecular structure of \([\text{Zn(S}_2\text{CN(Me)(CH}_2\text{)}_3\text{N(Me)}_2])\) (3). (b) Structure showing the polymeric linkage.

\[
\begin{align*}
\text{S(1)}-\text{Zn}(1) & \quad 2.3398(15), \quad \text{S(2)}-\text{Zn}(1) \quad 2.6281(14), \quad \text{S(3)}-\text{Zn}(1) \quad 2.3967(14), \quad \text{S(4)}-\text{Zn}(1) \\
& \quad 2.52891(14), \quad \text{C(1)}-\text{S}(2) \quad 1.713(6), \quad \text{C(1)}-\text{S}(1)1.739(5), \quad \text{C(2)}-\text{N}(1) \quad 1.468(6), \quad \text{S(1)}-\text{Zn}(1)-
\end{align*}
\]

\[
\begin{align*}
& \quad \text{S(3)} \quad 129.27(5), \quad \text{S(1)}-\text{Zn}(1)-\text{S}(4) \quad 104.41(5), \quad \text{S(3)}-\text{Zn}(1)-\text{S}(4) \quad 72.77(5), \quad \text{S(1)}-\text{Zn}(1)-
\end{align*}
\]

\[
\begin{align*}
& \quad \text{S(2)} \quad 72.74(5), \quad \text{S(3)}-\text{Zn}(1)-\text{S}(2) \quad 96.51(5), \quad \text{S(4)}-\text{Zn}(1)-\text{S}(2) \quad 163.94(5), \quad \text{Zn}(1)-\text{N}(2) \\
& \quad 2.115(5).
\end{align*}
\]
2.1.3 AACVD deposition of ZnS thin films from \( \text{bis(trimethylethylene-/-propylenediaminodithiocarbamato)zinc(II)} \) complexes 
\[ \text{[Zn(S}_2\text{CN(Me)(CH}_2\text{)}_n\text{N(Me)}_2\text{)}_2] (n =2 or 3) \]
The complexes were prepared as described in the experimental section. Both compounds are white solids soluble in most organic solvents on heating. These compounds are air and moisture stable for the period of several months.

2.1.4 TGA of \( \text{bis(trimethylethylene-/-propylenediaminodithiocarbamato)zinc(II)} \) complexes

TGA of the \( \text{bis(trimethylethlenedianimidothiocarbamato)zinc(II)} \) shows a very small mass loss, under 100 °C, and then a one major step loss, just below 200 °C, as in (Figure 2-4 (a)) leaving a 60% residue, which is considerably higher than the calculated value 22% . \( \text{bis(trimethylpropylenediaminodithiocarbamato)zinc(II)} \) shows a clean one step mass loss of around 80%. The remaining 20% residue is close to the calculated value 21.7%, for ZnS, (Figure 2-4 (b)). The difference in the decomposition behaviour of ethylene and propylene complexes is this case is unusual as there is no such difference with cadmium or other metal complexes (see sections 2.2.3, 3.1.1,..., etc).

![TGA diagram of: (a) [Zn(S2CN(Me)(CH2)2N(Me)2)] and (b) [Zn(S2CN(Me)(CH2)3N(Me)2)].](image-url)
2.1.5 Deposition of ZnS thin films

Deposition of ZnS thin films was carried out onto glass substrates by AACVD at different temperatures to compare the effect of temperature on the decomposition behaviour of the precursors and the morphology or phase of the deposited films. The deposition was carried out at 300, 400 and 500 °C. Full experimental details including the solvent used and the flow rate etc. are given in the experimental section.

2.1.5.1 p-XRD of ZnS

p-XRD of ZnS thin films deposited from bis(trimethylethylenediaminodithiocarbamato)zinc(II) at different temperature is shown in Figure 2-5. Very thin amorphous films were deposited at 300 °C whereas good quality crystalline films were deposited at 400 °C.

Figure 2-5: p-XRD pattern of films deposited by AACVD from [Zn(S₂CN(Me)(CH₂)₂N(Me)₂)₂] at 300 °C, 400 °C and 500 °C. Peaks indexed to hexagonal ZnS (ICDD card no. 01-080-0007).

p-XRD of these films showed the bands along (100), (002), (101), (110), (103) and (112) corresponding to the hexagonal phase of ZnS. The films deposited at 500 °C
were also hexagonal phase of ZnS but the p-XRD bands were comparatively broader than those deposited at 400 °C indicating the smaller size of crystallites.

The films deposited from \( \text{bis(trimethylpropylenediaminodithiocarbamato)zinc(II)} \) at different temperatures behaved similar to those deposited from \( \text{bis(trimethylethylene-diaminodithiocarbamato)zinc(II)} \). At 300 °C p-XRD showed a broad hump indicating either the deposition of very thin films or amorphous material. The films deposited at 500 °C were much more crystalline as compared to those observed from \( \text{bis(trimethylethylene-diaminodithiocarbamato)Zn(II)} \) and showing a strong indication of preferred orientation along 002 plane (Figure 2-6). The films deposited at lower temperature of 300 °C shows relatively low intensity peaks as compared to the films deposited at higher temperature of 400 °C and 500 °C. All peaks correspond to hexagonal phase of ZnS but with two different ICDD numbers.

Figure 2-6: p-XRD pattern of films deposited by AACVD from \([\text{Zn(S}_2\text{CN(Me)(CH}_2\text{)}_3\text{N(Me)}_2\text{)}_2]\) at 300 °C, 400 °C and 500 °C. Peaks indexed to mixture of hexagonal ZnS (ICDD card no. 04-008-7254) and (green) hexagonal ZnS (ICDD card no. 01-080-0007).
2.1.5.2 SEM of ZnS thin films
The films deposited at 300°C from bis(trimethylene diamino dithiocarbamato)zinc(II) showed only traces of very small crystallites whereas those deposited at 400 °C showed different shaped crystallites with large size distribution (Figure 2-7 (a) and (b) showing different magnifications). At 500 °C, a mixture of spherical crystallites and large worm like structures were observed. The diameter of spherical crystallites range from 300 nm to 600 nm whereas the size of worms was approximately 4 µm (Figure 2.8 (a) and (b) with different magnifications).

Figure 2-7: SEM images of ZnS thin films deposited from [Zn(S2CN(Me)(CH2)2N(Me)2)2] at 400 °C by AACVD.

Figure 2-8: SEM images of ZnS thin films deposited from [Zn(S2CN(Me)(CH2)2N(Me)2)2] at 500 °C by AACVD.
The films deposited from \textit{bis}(trimethylpropylenediaminodithiocarbamato)zinc(II) at 300 °C again showed no crystallites but those deposited at 400 °C showed random shape crystallites with the size ranging from 1µm to 100 nm (Figure 2-9 (a)) in a background of densely packed spherical nanoparticles with approximate size of 50 nm (Figure 2-9 (b)).

![Figure 2-9](image1.png)

Figure 2-9: SEM images of ZnS deposited from \([\text{Zn(S}_2\text{CN(Me)(CH}_2)_3\text{N(Me)}_2\text{)}_2]\) at 400 °C by AACVD.

![Figure 2-10](image2.png)

Figure 2-10: SEM images of ZnS deposited from \([\text{Zn(S}_2\text{CN(Me)(CH}_2)_3\text{N(Me)}_2\text{)}_2]\) at 500 °C by AACVD.

SEM images of thin films deposited at 500 °C from \textit{bis}(trimethylpropylenediaminodithio-carbamato)zinc(II) showed densely packed spherical crystallites with varying sizes ranging from 1µm to 200 nm (Figure 2-10).
(a)). At a higher magnification these crystallites appear to be clusters of small nanoparticles (Figure 2-10 (b)).

2.1.5.3 Atomic Force Microscopy of ZnS thin films

The surface topography of the deposited thin films were studied by atomic force microscopy. AFM of films deposited at 400 °C from bis(trimethylethlenediaminodithiocarbamato)zinc(II) is shown in Figure 2-11 with 2D and 3D images. Figure 2-11 shows a height of roughness is 191 nm.

![AFM images of ZnS thin films deposited from bis(trimethylethlenediaminodithiocarbamato)Zn(II) at 400 °C onto glass substrates in 2D (showing 2.0 µm/div) and 3D, and (b) Root Mean Square height of crystallisation in the ZnS thin films deposited at 400 °C.](image)

Figure 2-11: (a) AFM images of ZnS thin films deposited from bis(trimethylethlenediaminodithiocarbamato)Zn(II) at 400 °C onto glass substrates in 2D (showing 2.0 µm/div) and 3D, and (b) Root Mean Square height of crystallisation in the ZnS thin films deposited at 400 °C.
AFM of the films deposited from \textit{bis}(trimethylethylenediaminodithiocarbamato)zinc(II) at 500 °C (Figure 2-12 (a, b)) show a comparatively smoother surface with a height of roughness (roughly the height of roughness of depositions) is 103 nm.

![AFM image](image)

Figure 2-12: (a) AFM images of the ZnS thin films deposited at 500 °C from \textit{bis}(trimethylethylenediaminodithiocarbamato)zinc(II) onto glass substrates in 2D (showing 2.0µm/div) and 3D and (b) Root Mean Square of height of crystallisation in the ZnS thin films deposited at 500 °C.

Similarly the AFM images and root mean square height of crystallisation of the ZnS thin films deposited from \textit{bis}(trimethylpropylenediaminodithiocarbamato)Zn(II) at 400 and 500 °C are shown in Figure 2-13 and Figure 2-14. The films deposited at 400 °C show a height of roughness is 73.5 nm which is much smaller than compared...
to those deposited at 500 °C with a height of roughness is 126 nm or those deposited from bis(trimethylethylenediaminodithiocarbamato)zinc(II) at either temperature.

Figure 2-13: (a) AFM images of the ZnS thin films deposited from bis(trimethylpropylenediaminodithiocarbamato)zinc(II) at 400 °C in 2D (showing 2.0µm/div) and 3D and (b) Root Mean Square of height of crystallisation of ZnS thin films deposited at 400 °C.
Figure 2-14: (a) AFM images of the ZnS thin films deposited from bis(trimethylpropylenediaminodithiocarbamato)Zn(II) at 500 °C in 2D (showing 2.0µm/div) and 3D and (b) Root Mean Square of height of crystallisation of ZnS thin films at 500 °C.

2.2 Cadmium sulfide

Cadmium sulfide is a direct band gap semiconductor (gap 2.42 eV). It is sensitive to visible and near infrared light. The conductivity of CdS increases when irradiated with light (leading to uses as a photoresistor) when combined with a p-type semiconductor it forms the core component of a photovoltaic (solar) cell and a CdS/Cu$_2$S solar cell was one of the first efficient cells to be reported (1954).\textsuperscript{39,40} When doped with for example Cu$^+$ ("activator") and Al$^{3+}$ ("coactivator") CdS luminesces under electron beam excitation (cathodoluminescence) and is used as phosphor.\textsuperscript{41} Both polymorphs are piezoelectric and the hexagonal form is also pyroelectric\textsuperscript{42} and electroluminescent.\textsuperscript{43} CdS crystal can act as a form solid state
laser.\textsuperscript{44,45} In thin-film form, CdS can be combined with other layers for use in certain types of solar cells.\textsuperscript{46} CdS was also one of the first semiconductor materials to be used for thin-film transistors (TFTs).\textsuperscript{47a} It exists in two crystallographic structures. The more stable hexagonal wurtzite structure (found in the mineral Greenockite) and the cubic zinc blend structure (found in the mineral Hawleyite). In both of these forms the cadmium and sulphur atoms are four coordinate (Figure 2-15).\textsuperscript{47(b,c)}

![Figure 2-15: (a) Structure of hawleyite and (b) Structure of greenockite.\textsuperscript{47(b,c)}](image)

### 2.2.1 Cadmium sulfide thin films

The growth of II-VI thin films by a chemical method became practical with Manasevit's use of volatile metal alkyls such as dimethylcadmium (Me\textsubscript{2}Cd) or dimethylzinc (Me\textsubscript{2}Zn) in a combination with H\textsubscript{2}S, H\textsubscript{2}Se, or Me\textsubscript{2}Te delivered in dihydrogen as a carrier gas effectively inventing and defining the process of MOCVD. Many films were grown including of ZnS, ZnSe, CdS, CdSe, and CdTe.\textsuperscript{48} The method involves the delivery of both a metal alkyl and a chalcogenide source in the vapour phase to a mixing chamber and onward to a deposition zone; particulate material can form before the vapours reach the heated substrate, sometimes termed ‘pre-reaction’. To overcome some of these problems new precursors were developed to control volatility, reduce toxic hazard, improve the quality of the grown layers and reduce the temperature required for growth. These precursors include alternate chalcogenide precursors, metal alkyl adducts, and single-source precursors. Single
source precursors are the most favourite precursors for the growth of thin films by CVD method. Several classes of single source precursors have been developed during the last two decades including dithiocarbamates, xanthates, thioureas, thiosemicarbazides, dithiocarbazates, dithiophosphates, dithiophosphinates, and dithioimidodiphosphinates. A review by Gleizes gives a detailed account on the use of single source precursors by CVD (Chemical Vapour Deposition) method.

Takahashi deposited CdS using dimethylthiophosphinates \([M(S_2PMe_2)_2]\) (M = Cd or Zn) and Evans and Williams reported that highly orientated CdS films could be grown using the diethylthiophosphinates as precursors. O’Brien et al. deposited CdS and ZnS films from \([Cd(S_2P^Bu_2)_2]_2\) and \([Zn(S_2P^Bu_2)_2]_2\) respectively using a home made cold-wall low-pressure reactor. Monothiocarbamates such as Cd\((SOCNEt_2)_2\) have also been used for the preparation of CdS films by LP-MOCVD. Also compounds of the type \(M(SOCCH_3)_2TMEDA\) (M = Zn, Cd; TMEDA = \(N,N',N''-\)tetramethyl-ethylenediamine) have been used to grow CdS and ZnS by AACVD and by laser-assisted CVD. Recently Aerosol Assisted (AA) CVD have been used to grow CdS thin films from cadmium complex of dimorpholinodithioacetylacetonate.

The dithiocarbamate complexes derived from trimethylpropylenediamine were synthesized by a comproportionation reaction. This complex showed a different structure from the dimers and is a weakly bonded polymer, as shown in Figure 2-16. The compound is apparently more volatile than the simpler dithiocarbamates and has successfully been used in deposition experiments to deposit CdS thin film on glass or GaAs substrates at 350°C.

Another related class of compounds \(N\)-alkyldithiocarbamato \([M(S_2CNHR)_2]\) have potential as precursors. Very little was reported about these complexes due to the supposition that these complexes are not very stable and were also expected to be less volatile, and consequently less suitable as single-source CVD precursors. Recently O’Brien et al. have synthesized a series of complexes of cadmium or zinc with varying alkyl chain lengths \(M(S_2CNHR)_2\) (M = Cd(II) Zn(II); R = \(C_2H_5\), \(C_4H_9\), \(C_6H_{13}\), \(C_{12}H_{25}\))

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The condensation of the primary amines with carbon disulfide in the presence of metal salts produced \([\text{M}(\text{S}_2\text{CNHR})_2] \) (\( \text{M} = \text{Cd(II)} \) or \( \text{Zn(II)} \)) in a reasonable purity with good yield. Most of these complexes were only sparingly soluble in organic solvents.

2.2.2 Synthesis and X-ray structures of \([\text{Cd}(\text{S}_2\text{CN})(\text{CH}_2)_2\text{N(Me)}_2)_2] \) (4) \n\([\text{Cd}(\text{S}_2\text{CN})(\text{CH}_2)_2\text{N(Me)}_2)_2] \) (5)

Compound (4) was synthesised by the reaction of \( N,N,N \)-trimethylethylene diamine with carbon disulfide and with cadmium salt in methanol at room temperature (full details in experimental section). The complex was crystallised from chloroform to give small cubic crystals. The compound is a yellowish white solid soluble in most organic solvents and is air and moisture stable for the period of several months. Equation 2-2. \( \text{Bis}(N,N,N\text{-trimethylpropylenediaminodithiocarbamato})\text{cadmium(II)} \) (5) was prepared by the same method as used for compounds (2-4). The compound was crystallised from hot chloroform to give white crystals. Structures of both compounds was determined by X-ray crystallography.

2.2.2.1 Structure of \([\text{Cd}(\text{S}_2\text{CN})(\text{CH}_2)_2\text{N(Me)}_2)_2] \) (4)

The Crystal data and structure refinements of compound (4) are given in Table 2-4. The molecular structure of the complex is shown inFigure 2-17. The structure is based on a polymer similar to that reported for the related cadmium compound, \( \{\text{MeCdS}_2\text{CN(Me)(CH}_2)_3\text{N(Me)}_2\}_n \).\(^{31}\)
Figure 2-17: (a) Molecular structure of [Cd(S₂CN(Me)(CH₂)₂N(Me)₂)] (4) and (b) structure showing the polymeric linkage.

**Selected bond lengths (Å) and angles (°):**  
(Cd(1)-N(4)#1, 2.354(3); Cd(1)-S(2), 2.5567(12); Cd(1)-S(3), 2.6184(11); Cd(1)-S(4), 2.6381(11); Cd(1)-S(1), 2.6640(11); N(4)-Cd(1)#2, 2.354(3); N(4)#1-Cd(1)-S(2), 123.58(9); N(4)#1-Cd(1)-S(3), 96.89(9); S(2)-Cd(1)-S(3), 139.13(4); N(4)#1-Cd(1)-S(4), 102.13(8); S(2)-Cd(1)-S(4), 104.01(3); S(3)-Cd(1)-S(4), 69.00(3); N(4)#1-Cd(1)-S(1), 98.89(9); S(2)-Cd(1)-S(1), 69.49(3); S(3)-Cd(1)-S(1), 101.42(4).
The structure consists on \([\text{Cd}(S_2CN(\text{Me})(\text{CH}_2)_2N(\text{Me})_2)_2]\) molecule which are interlinked by Cd-N interactions. The Cd-N bond distances (2.35 Å) are larger than those observed for Zn-N (2.11 Å) as expected due to the larger atomic radius of cadmium. Each cadmium atom is coordinated by four sulphur atoms from two ligands (bidentate) and a nitrogen atom from the neighbouring molecule’s amino group.

Table 2-4: Crystal data and structure refinement for \([\text{Cd}(S_2CN(\text{Me})(\text{CH}_2)_2N(\text{Me})_2)_2]\) (4).

<table>
<thead>
<tr>
<th>Compound</th>
<th>([\text{Cd}(S_2CN(\text{Me})(\text{CH}_2)_2N(\text{Me})_2)_2]) (4)</th>
</tr>
</thead>
<tbody>
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<td><strong>Empirical</strong></td>
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<td><strong>Formula weight</strong></td>
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<tr>
<td><strong>Crystal system, unit cell dimensions</strong></td>
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</tr>
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</tr>
<tr>
<td><strong>b = 16.1142(12) Å</strong></td>
<td>beta = 100.8180(10) °</td>
</tr>
<tr>
<td><strong>c = 12.8519(10) Å</strong></td>
<td>gamma = 90 °</td>
</tr>
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<td><strong>Volume</strong></td>
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<td><strong>Z, Calculated</strong></td>
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</tr>
<tr>
<td><strong>Absorption</strong></td>
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</tr>
<tr>
<td><strong>R indices (all)</strong></td>
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</tr>
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</tr>
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<td><strong>Reflections</strong></td>
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<td><strong>Limiting indices</strong></td>
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</table>

### 2.2.2.2 Synthesis and characterisation of \([\text{Cd}(S_2CN(\text{Me})(\text{CH}_2)_3N(\text{Me})_2)_2]\) (5)

The crystal refinement data is given in Table 2-5 and the molecular structure is shown in Figure 2-18. The structure is similar to that of compound (4). There were no unusual bond lengths and angles.
Figure 2-18: (a) Molecular structure of \([\text{Cd}(\text{S}_2\text{CN}(\text{Me})(\text{CH}_2)_3\text{N}(\text{Me})_2)_2]\) (5) and (b) structure showing the polymeric linkage.

**Selected bond lengths (Å) and angles (°):**
- Cd(1)-N(4)#1,2.337(5)
- Cd(1)-S(3) 2.5475(18)
- Cd(1)-S(2), 2.6002(18)
- Cd(1)-S(1), 2.6469(19)
- Cd(1)-S(4) 2.6954(18)
- N(4)-Cd(1)#2, 2.337(5)
- N(4)#1-Cd(1)-S(3), 107.88(14)
- N(4)#1-Cd(1)-S(2), 120.81(14)
- S(3)-Cd(1)-S(2), 131.17(6)
- N(4)#1-Cd(1)-S(1), 99.01(14)
- S(3)-
Cd(1)-S(1), 108.80(6); S(2)-Cd(1)-S(1), 68.92(5); N(4)#1-Cd(1)-S(4), 93.70(14); S(3)-Cd(1)-S(4), 69.51(5); S(2)-Cd(1)-S(4),102.05(5); S(1)-Cd(1)-S(4), 166.97(5).

Table 2-5: Crystal data and refinement for [Cd(S_2CN(Me)(CH_2)_3N(Me)_2)] (5).

<table>
<thead>
<tr>
<th>compound</th>
<th>[Cd(S_2CN(Me)(CH_2)_3N(Me)_2)] (5)</th>
</tr>
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<tr>
<td>Empirical formula</td>
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</tr>
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</tr>
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</tr>
<tr>
<td>Absorption coefficient</td>
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<tr>
<td>Goodness-of-fit on F²</td>
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</tr>
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<td>Final R indices [I&gt;2σ(I)]</td>
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<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.0481, wR₂ = 0.1029</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.701 and -0.534 e.A⁻³</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>9015 / 4656 [R(int) = 0.0606]</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-10≤h≤10, -16≤k≤15, -15≤l≤14</td>
</tr>
</tbody>
</table>

2.2.3 TGA of bis(trimethylethylene-/propylenediaminodithiocarbamato)-cadmium(II) complexes

TGA of the bis(trimethylethyleneaminodithiocarbamato)cadmium(II) shows a very small mass loss around 150 °C and then a major one step loss just around 200 °C, (Figure 2-19 (a)), leaving a 28% residue which is close to the calculated value 31%. Bis(trimethylpropylenediaminodithiocarbamato)cadmium(II) shows a clean one step mass loss of around 80% similar to that observed for bis(trimethylpropylenediaminodithiocarbamato)zinc(II). The remaining 20% residue is lower than the calculated value 29%. (Figure 2-19 (b)). The decomposition behaviour of ethylene cadmium complex is significantly different than that of corresponding
zinc complex. The reason may be that the zinc complex gets easily oxidised (see X-ray structure of zinc complex) under atmospheric conditions and gives zinc oxide in addition to zinc sulfide.

Figure 2-19: TGA diagram of (a) [Cd(S₂CN(Me)(CH₂)₃N(Me)₂]₂ and (b) [Cd(S₂CN(Me)(CH₂)₂N(Me)₂]₂.

2.2.4 AACVD deposition of CdS thin films from [Cd(S₂CN(Me)(CH₂)ₙN(Me)₂]₂ (n =2 or 3)

Bis(trimethylethylene-/propylenediaminodithiocarbamato)Cd(II) complexes are whitish solids soluble in most organic solvents on heating.

2.2.4.1 p-XRD patterns of CdS thin films

p-XRD patterns of CdS thin films deposited from the bis(trimethylethylenediaminodithiocarbamato)cadmium(II) CdS thin films were deposited onto glass substrates from bis(trimethylethylenediamino-dithiocarbamato)cadmium(II) by AACVD at 300, 400 and 500 °C. p-XRD patterns of the films deposited at all three temperatures are shown in Figure 2.20. Deposition at all temperature gives hexagonal phase of CdS. The only obvious difference in the p-XRD patterns is that films
deposited at 300 °C give slightly broader peaks than those deposited at 400 or 500 °C. This broadening of peaks at lower temperature may be due to the smaller size of crystallites at lower temperatures and the size increases as the deposition temperature is increased which is shown by sharper p-XRD peaks at 400 and 500°C.

Figure 2-20: p-XRD pattern CdS thin films deposited from [Cd(S₂CN(Me)(CH₂)₂N(Me)₂)₂] by AACVD at 300 °C, 400 °C and 500 °C. Peaks indexed to hexagonal CdS (ICDD card No. 01-077-2306).

2.2.4.2 p-XRD patterns of CdS thin films deposited from the bis(trimethylpropylenediamino-dithiocarbamato)cadmium(II)

Thin films of CdS were deposited from bis(trimethylpropylenediamino-dithiocarbamato)cadmium(II) at 300, 400 and 500 °C. Deposition at all temperature produced polycrystalline hexagonal CdS thin films. Films deposited at higher temperature of 500 °C showed some preferred orientation along (002) plane. Figure 2.21 show the p-XRD pattern for the films deposited at all three temperatures. The films deposited at lower temperature of 300 °C shows relatively low intensity peaks as compared to the films deposited at higher temperature of 400 °C and 500 °C.
Figure 2-21: p-XRD patterns of CdS thin films deposited from [Cd(S₂CN(Me))(CH₂)₂N(Me)₂] at 300 °C, 400 °C and 500 °C onto glass substrates by AACVD. Peaks indexed to hexagonal CdS (ICDD card No. 01-075-1545).

2.2.4.3 SEM of CdS thin films deposited from bis(trimethylethlenediaminodithiocarbamato)cadmium(II)

SEM images of thin films of CdS deposited from bis(trimethylethlenediaminodithiocarbamato)cadmium(II) at 300 °C are shown in Figure 2-22. There is an uneven growth of CdS crystallites on the substrate. Patches of CdS are grown onto the glass substrate with some completely empty spaces. The crystallites have random shape with their size ranging from less than a micron to several microns forming clusters of small crystals.

The SEM images of the films deposited at 400 °C showed a similar behaviour but with a smaller size distribution (Figure 2-23).
Figure 2-22: SEM images of CdS thin films deposited from [Cd(S₂CN(Me)(CH₂)₂N(Me)₂)₂] at 300 °C by AACVD.

Larger crystallites are deposited on the smoother background of nanocrystalline CdS (Figure 2.22 (b)). The spherical nanocrystals with approximate diameter of 50 nm cluster to form some larger particles.

Figure 2-23: SEM images of CdS thin films deposited from [Cd(S₂CN(Me)(CH₂)₂N(Me)₂)₂] at 400 °C by AACVD.

CdS films grown at 500 °C showed a much more even surface than those deposited at 300 or 400 °C (Figure 2-24). SEM images show that the films consist of small spherical particles which are densely packed to given an even film on glass substrates.
Figure 2-24: SEM images of CdS thin films deposited from [Cd(S₂CN(Me)(CH₂)₂N(Me)₂)] at 500 °C by AACVD.

2.2.4.4 SEM of CdS thin films deposited from bis(trimethylpropylenediaminodithiocarbamato)cadmium(II)

SEM micrographs of CdS thin films deposited from bis(trimethylpropylenediaminodithiocarbamato)cadmium(II) at 300 °C are shown in Figure 2-25. The image shows a deposition of much smoother film of CdS. The films consist of close to spherical CdS nanoparticles densely packed on the glass substrate.

Figure 2-25: SEM images of CdS deposited from [Cd(S₂CN(Me)(CH₂)₃N(Me)₂)] at 300 °C by AACVD.
Figure 2-26 (b) shows a higher magnification image, the size of nanoparticles is approximately 100 nm. These films are much more uniform with even surface than those deposited from bis(trimethylethynediaminodithio-carbamato)cadmium(II) at all temperatures.

Figure 2-26: SEM images of CdS thin films deposited from [Cd(S₂CN(Me)(CH₂)₂N(Me)₂)_2] at 400 °C by AACVD.

The SEM images of CdS films deposited at 400 °C showed a nanocrystalline tubular material forming a network (Figure 2-26 (a-b)). The higher magnification image (Figure 2-26 (b)) clearly shows the formation of a network to form porous films with an approximate size of 100 nm pores. There is no such example of CdS porous films in the literature.

The SEM images of films deposited at 500 °C showed the deposition of hexagonal crystals densely packed on the substrate to give an even film (Figure 2-27). The average size of the crystallites is approximately 500 nm Figure 2-27 (b). These are the only CdS films in this class of precursors which show the growth of crystals with regular shapes. Their highly crystalline nature was also showed by the sharper p-XRD peaks.
Figure 2-27: SEM images of CdS thin films deposited from [Cd(S$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$)$_2$] at 500 °C by AACVD.

2.2.4.5 AFM of CdS thin films deposited from bis(trimethylethylenediaminodithiocarbamato)cadmium(II)

The AFM images of the CdS films deposited from bis(trimethylethylenediaminodithio-carbamato)cadmium(II) at 300, 400 and at 500 °C are shown in Figure 2-28, Figure 2-29 and Figure 2-30 respectively.
Figure 2-28: (a) AFM images of the CdS thin films deposited from bis(trimethylethylene-diaminodithiocarbamato)cadmium(II) at 300 °C in 2D (showing 2.0µm/div) and (b) in 3D, the Root Mean Square of height of crystallisation.

The films deposited at 300 °C show random crystallites lying on a much smoother surface based on an even growth of smaller spherical nanocrystals.

The height of roughness of the surface is close to 80 nm, which is smaller than the films grown at either 400 °C (120 nm) (Figure 2-29) or 500 °C (118 nm) (Figure 2-30).
Figure 2-29: (a) AFM images of the CdS thin films deposited from bis(trimethylene-diaminodithiocarbamato)cadmium(II) at 400 °C in 2D (showing 2.0µm/div) and (b) in 3D, the Root Mean Square of height of crystallisation.

The AFM images in Figure 2-29 and Figure 2-30 clearly show the larger and more uniform size of crystallites as compared to the films grown at 300 °C.
Figure 2-30: (a) AFM images of the CdS thin films deposited from bis(trimethylethylene-diaminodithiocarbamato)cadmium(II) at 500 °C in 2D (showing 2.0µm/div) and (b) in 3D, the Root Mean Square of height of crystallisation.

2.2.4.6 AFM of CdS thin films deposited from bis(trimethylpropylene-diaminodithiocarbamato)cadmium(II).

The AFM images and the roughness of the CdS thin films deposited from bis(trimethylpropylenediaminodithio-carbamato)cadmium(II) at 300, 400 and 500 °C are shown in Figure 2-31 - 33.
Figure 2-31: (a) AFM images of the CdS thin films deposited from bis(trimethylpropylene-diaminodithiocarbamato)cadmium(II) at 300 °C in 2D (showing 2.0µm/div) and (b) in 3D, the Root Mean Square of height of crystallisation.

The films deposited at 300 and 500 °C show a similar height of roughness of 46-47 nm whereas the films deposited at 400 °C show a comparatively much smaller roughness (26 nm).
Figure 2-32: (a) AFM images of the CdS thin films deposited from bis(trimethylpropylene-diaminodithiocarbamato)cadmium(II) at 400 °C in 2D (showing 2.0µm/div) and (b) in 3D, the Root Mean Square of height of crystallisation.

Figure 2-33: (a) AFM images of the CdS thin films deposited from bis(trimethylpropylene-diaminodithiocarbamato)cadmium(II) at 500 °C in 2D (showing 2.0µm/div) and (b) in 3D, Root Mean Square of height of crystallisation.
2.3 Conclusion

Bs(trimethylethylene-/propylenediaminodithiocarbamato)-zinc/cadmium(II) complexes: [M(S₂CN(Me)(CH₂)ₙN(Me)₂)₂] (M = Zn or Cd; n = 2 or 3 have been synthesised and characterised by elemental analysis, NMR (¹H and ¹³C), and X-ray crystallography. All compounds are crystalline solids hence their structure was determined by single crystal X-ray crystallography. The compounds are air and moisture stable for months at room temperature. All four complexes (2-5) were used as single source precursors for the deposition of zinc or cadmium sulfide thin films by AACVD. All complexes deposited the corresponding metal sulfide thin films onto glass substrates. The films were deposited at different temperatures to investigate the effect of deposition temperature on the size and shape of crystallites. SEM and AFM images showed remarkable differences in morphology of ZnS and CdS in relation to changes in deposition temperature. Mostly zinc and cadmium sulfide thin films have been grown from single source precursors by LP-CVD method where volatility of the precursors is a big issue. This is the first time that a systematic study is carried out using diamino derivatives of thiocarbamato complexes to grow films by AACVD method where volatility of the precursors is not required. Both zinc and cadmium complexes are polymeric (see X-ray structures), hence unsuitable for LP-CVD method to deposit zinc or cadmium sulfide films whereas these complexes are perfectly suitable to deposit films by AACVD method.
2.4 References


Chapter 3: Deposition of transition metal sulfides

Chapter 3 describe the use of newly synthesised transition metal complexes [M(S₂CN(Me)(CH₂)ᵣN(Me)₂)] (M = Cu, Ni; n = 2, 3) [Co(S₂CN(Me)(CH₂)ᵣN(Me)₂)] (n = 2, 3) [Ag(S₂CN(Me)(CH₂)₃N(Me)₂)] as precursors for the deposition of corresponding metal sulfide thin films onto glass substrates by AACVD. A detailed introduction of each material is also given with complete characterization of thin films by p-XRD, SEM and AFM.
3.1 Copper sulfide

Transition metal sulfides are of interest for their application as catalysts, heavy metal sponge absorbents, chemical sensors, luminescent devices, superconductors and also in dry lubrication and ionic intercalation in secondary batteries.\textsuperscript{1-5} Copper sulfide thin films and nanoparticles have been investigated for p-type semiconductors in solar cells,\textsuperscript{6,7} nanoscale switches\textsuperscript{8} and as cathodic materials in lithium rechargeable batteries.\textsuperscript{9} The study of copper sulfide thin films has given much attention due to numerous technological applications in achievement of solar cells\textsuperscript{10}, in photochemical conversion of solar energy as solar absorber coating\textsuperscript{11}, as selective radiation filters on architectural windows for solar control in the warm climates\textsuperscript{12}, as electroconductive coatings deposited on organic polymers\textsuperscript{13}. Copper sulfide is found to exist in two forms, at room temperature, as copper-rich and copper-poor phases. Copper-rich phases include: chalcocite (Cu$_2$S), djurleite (Cu$_{31}$S$_{16}$ or Cu$_{1.94}$S), digenite (Cu$_9$S$_5$ or Cu$_{1.8}$S) and anilite (Cu$_7$S$_4$ or Cu$_{1.75}$S) and copper poor phase as covellite (CuS).\textsuperscript{14} Covellite has one-third of its metal ions surrounded by three neighbouring S atoms at the corners of a triangle and the remainders have four S neighbours arranged in tetrahedral coordination. So far, Cu$_x$S thin films have been prepared by various techniques such as chemical bath deposition (CBD)\textsuperscript{12,15-20}, vacuum evaporation\textsuperscript{21}, activated reactive evaporation\textsuperscript{22}, spray pyrolysis\textsuperscript{23,24}, and photochemical deposition (PCD)\textsuperscript{25}, RF-reactive sputtering\textsuperscript{26}, successive ionic layer adsorption and reaction\textsuperscript{27}, chemical bath deposition\textsuperscript{28} and chemical vapour deposition\textsuperscript{29}. In our POB group continuing search for potential single source precursors we have studied metal complexes of dichalcogenocarbamates,\textsuperscript{30-35} dichalcogenoimidodiphosphinates,\textsuperscript{36-39} and dichalcogenophosphinates\textsuperscript{40,41} as suitable precursors for deposition of metal chalcogenide thin films by MOCVD.

In our lab good quality Cu$_7$S$_4$ nanoparticles and the AACVD deposition of CuS$_2$ and Cu$_2$S thin films were obtained\textsuperscript{42} from a 1,1,5,5-tetra-\textit{iso}-propyl-2-thiobiuret [Cu(SON(CN\textit{Pr$_2$})$_2$)].\textsuperscript{43} Powder X-ray diffraction (p-XRD) patterns of the thin films showed the deposition of a mixture of cubic CuS$_2$ and hexagonal Cu$_2$S solution at all temperatures. Scanning Electron Microscopy (SEM) of copper sulfide films showed spherical crystallites from reaction at 280 °C, cuboids at 320 °C and plate like
crystallites between 360 and 400 °C. Transmission Electron Microscopy (TEM) of material scratched from thin films showed nanoplates of copper sulfides with 25-30 nm size.

3.1.1 TGA of [M(S$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$)$_n$] (M= Ag; n=1), (M = Cu, Ni; n=2), (M= Co; n= 3)

Thermogravimetric analysis of [M(S$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$)$_n$] (M= Ag; n=1), (M = Cu, Ni; n=2), (M= Co; n= 3) are shown in Figure 3-1. All four complexes decompose in a clean single step. The copper complex decomposed to give about 19% residue which is close to the calculated value 21.5%. Silver complex gives the highest amount of residue 40% which is a bit lower than the calculated value for silver sulfide 46.8%. Nickel and cobalt complexes give 20% and 17% residue respectively which are close to their calculated values 20.6% and 14% respectively. A clear difference in the decomposition temperature can be noted from the TGA pattern that both copper and silver complexes decompose around 200 °C whereas the other two nickel and cobalt complexes decompose at 300 °C. These results shows that the nickel and cobalt complexes are thermodynamically more stable than the complexes of copper and silver.

![Figure 3-1: TGA for [M(S$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$)$_n$] (M= Ag; n=1), (M = Cu, Ni; n=2), (M= Co; n= 3). (a) copper complex (b) silver complex (c) nickel complex and (d) cobalt complex.](image-url)
3.1.2 Deposition of CuS thin films from bis(trimethylpropylene-diaminodithiocarbamato)copper(II): \([\text{Cu}(\text{S}_2\text{CN}(\text{Me})(\text{CH}_2)_3\text{N(Me)}_2)_2]\) by AACVD Method

*Bis*(trimethylpropylenediaminodithiocarbamato)Cu(II) complex was prepared by the reaction of Cu(NO$_3$)$_2$ . 2.5H$_2$O in with N,N,N-trimethylpropylene-diamine and carbon disulfide in a water/methanol mixture at room temperature. Equation 2-2. The product was obtained as a dark colour solid. Repeated attempts to recrystallise the compound to get good enough quality crystals for X-ray structures were unsuccessful. The compound is stable at room temperature for long periods of time.

3.1.2.1 p-XRD of copper sulfide thin films deposited from bis(trimethylpropylendiaminodithiocarbamato)copper(II)

Copper sulfide thin films were deposited at three different temperatures (300, 400, 500 °C) by AACVD method. The p-XRD pattern for the films deposited at all temperatures are shown in Figure 3-2. The p-XRD pattern of the films deposited at all temperatures show the deposition of polycrystalline films of a mixture of tetragonal Cu$_2$S and rhombohedral Cu$_9$S$_5$. There is no significant difference in all three patterns except a clear peak shown by the films deposited at 400 °C along (112) plane. Also the films deposited at 400 °C show a pattern with comparatively weaker peaks which may be due the deposition of smaller crystallites.
Figure 3-2: XRD diagram of films deposited by AACVD from [Cu(S₂CN(Me)(CH₂)₃N(Me)₂)₂] at 300 °C, 400 °C, and 500 °C. Peaks indexed to mixture of tetragonal Cu₂S (ICDD card No. 01-072-1071) and (green) rhombohedral, digenite Cu₉S₅ (ICDD card no. 00-023-0962).

3.1.2.2 SEM of copper sulfide thin films deposited from bis(trimethylpropylenediaminodithiocarbamato)copper(II)

SEM images of the films deposited at 300 °C are shown in Figure 3.3. Films with even surface are deposited. The higher magnification image shows the size of the crystallites as close to 500 nm (Figure 3-3 (b)). The crystallites appear to close to hexagonal shapes with narrow size distribution.

Figure 3-3: SEM images (a, b with different magnification) of copper sulfide deposited from [Cu(S₂CN(Me)(CH₂)₃N(Me)₂)₂] by AACVD method at 300 °C.
The SEM images of the films deposited at 400 °C showed a clear distinction in the shape of crystallites (Figure 3-4). The films deposited at 400 °C showed the plate shape crystallites with approximate lengths of 3 µm. The crystallites were evenly distributed throughout the surface give it a smooth morphology.

![SEM images](image1)

Figure 3-4: SEM images (a, b with different magnification) of copper sulfide deposited from [Cu(S\(_2\)CN(Me)(CH\(_2\)\(_3\)N(Me)\(_2\))] by AACVD method at 400 °C.

The SEM images of the films deposited at 500 °C showed the surface composed of star shaped crystallites. These crystallites are evenly distributed over the surface to give a homogeneous morphology.

![SEM images](image2)

Figure 3-5: SEM images (a, b with different magnification) of copper sulfide deposited from [Cu(S\(_2\)CN(Me)(CH\(_2\)\(_3\)N(Me)\(_2\))] by AACVD method at 500 °C.
It is interesting to note the highly significant changes in the shape and size of crystallites deposited at different temperatures. It is quite obvious that the temperature is the main factor controlling the morphology of the copper sulfide films. Usually the size of crystals as well as the crystallinity of these materials increase at higher temperature, may be due to the fusion of smaller crystals and the annealing effect.

3.1.2.3 AFM of copper sulfide thin films deposited from bis(trimethylpropylenediaminodithiocarbamato)copper(II)

The AFM images, with their root mean height of crystallisation of the films deposited at 300 °C, 400 °C and 500 °C are given in Figure 3-6, Figure 3-7 and Figure 3-8, respectively. The films deposited at 300 °C show a smooth surface with round shape crystallites, as was, also, clear from SEM images. The height of roughness of the surface was close to 280 nm (Figure 3-6). Copper sulfide films deposited at 400 °C show an even smoother morphology, with the height of roughness is 159 nm (Figure 3-7). A clear difference emerged, in the morphology of the films deposited at 500 °C, which showed a surface composed of dense mass, with regular rows of some pattern (Figure 3-8). Again AFM showed very distinct morphologies of the copper sulfide films, depending upon the deposition temperature.
Figure 3-6: (a) AFM images (2D and 3D) of films deposited at 300 °C from bis(trimethylpro-pylenediaminodithiocarbamato)copper(II) and (b) Root Mean Square of height of crystallisation.

Figure 3-7: (a) AFM images (2D and 3D) of films deposited at 400 °C from bis(trimethylpropylenediaminodithiocarbamato)copper(II) and (b) Root Mean Square of height of crystallisation.
Figure 3-8: (a) AFM images (2D and 3D) of films deposited at 500 °C from bis(trimethylpropylenediaminodithiocarbamato)copper(II) and (b) Root Mean Square of height of crystallisation.

3.2 Silver sulfide

Silver sulfide has a band gap of 1 eV and has found uses in IR detectors, photosensitive materials for recording media, solar selective coatings and ion-selective electrode membranes. Silver rich silver sulfide thin films show applications for photoimaging and photodetection in the IR region. The Ag$_2$S/Ag junction has been found to be ohmic and this property was exploited by Terabe et. al. to create a nanodevice, quantized conductance atomic switch which can carry out basic logic operations. Silver sulfide is a mixed ionic and electronic conductor which exists in 3 phases; α-Ag$_2$S (acanthite) with a monoclinic structure stable up to 178 °C, β- Ag$_2$S (argentite) which has a bcc structure and stable between 178-600 °C and γ- Ag$_2$S having fcc structure and stable between 600-825 °C.

Thin films of silver sulfide have been prepared by various methods including chemical bath deposition, spray pyrolysis, thermal evaporation, sol-gel, successive ionic layer adsorption and reaction (SILAR), molecular beam epitaxy and electrochemical ion-exchange process. Silver(I)thiobenzoate
[Ag(SCOPh)] was used as a single molecule precursor to grow Ag$_2$S nanocrystals in hexadecylamine (HDA) solutions.\textsuperscript{70} Tang \textit{et. al.} have used this precursor to produce Ag$_2$S or mixtures of Ag$_2$S and Ag or pure Ag nanocrystals depending upon the precursor injection temperatures with tri-octylphosphine (TOP) as a solvent.\textsuperscript{71} They have also reported the formation of Ag$_2$S nanocrystal thin films when an aliquot of [Ag(SCOPh)] dissolved in TOP was added onto a preheated SiO$_2$/Si substrates.\textsuperscript{72} Silver films have applications in microelectronics,\textsuperscript{73} dopants in superconducting materials\textsuperscript{74} and as surface enhanced Raman active substrates.\textsuperscript{75} Physical vapour deposition methods such as vacuum evaporation,\textsuperscript{76} sputtering,\textsuperscript{77} electron beam evaporation\textsuperscript{78} pulsed laser deposition\textsuperscript{79} and molecular beam epitaxy\textsuperscript{80} have been used for the growth of silver films. O’Brien \textit{et al.}\textsuperscript{81} were the first to deposit silver sulfide thin films by a metal-organic chemical vapour deposition (MOCVD) method from a single source metal-organic precursor, tetraisopropyldithioimidodiphosphinato)silver(I) a trinuclear complex. Recently Ag$_2$S films deposited by electrodeposition onto silver substrates were investigated for the semi-conducting and photoelectrochemical properties.\textsuperscript{82}

3.2.1 Deposition of silver sulfide from trimethylpropylenediaminedithiocarbamato)silver(I) [AgS$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$]

Trimethylpropylenediaminedithiocarbamato)silver(I) was prepared by the method described in chapter 5. Freshly prepared compound is a white solid but changes color over the period of weeks. It is soluble in common organic solvents such as toluene, THF and chloroform. Equation 2-2.

3.2.1.1 p-XRD of Ag$_2$S thin films deposited by AACVD.

Silver sulfide thin films were deposited at three different temperatures and their p-XRD patterns were taken at each temperature. Figure 3-9 show the patterns of the films deposited at 300 °C, 400 °C and 500 °C. At 300 °C comparatively thin films were deposited which was clear from the p-XRD showing broad peaks. The films deposited at 400 °C gave very sharp peaks in their p-XRD pattern indicating the growth of crystalline films with larger size of crystallites. Similarly films deposited at higher temperature of 500 °C showed clear peaks for silver sulfide. The peaks in the
p-XRD patterns at all three temperature were indexed to the monoclinic Ag$_2$S (ICDD card No. 00-014-0072).

![p-XRD pattern of silver sulfide films deposited by AACVD from [AgS$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$] at 300 °C, 400 °C and 500 °C. Peaks indexed to monoclinic Ag$_2$S (ICDD card No. 00-014-0072).](image)

Figure 3-9: p-XRD pattern of silver sulfide films deposited by AACVD from [AgS$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$] at 300 °C, 400 °C and 500 °C. Peaks indexed to monoclinic Ag$_2$S (ICDD card No. 00-014-0072).

3.2.1.2 SEM of silver sulfide thin films from [AgS$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$]

SEM images of the films deposited at 300 °C from [AgS$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$] are given in Figure 3-10. The images show the deposition of a very thin film as was indicated by the p-XRD pattern. The film appear to be composed of granular crystallites with size range of about 50-100 nm forming clusters.
Figure 3-10: SEM images (a, b with different magnification) of silver sulfide deposited from $[\text{AgS}_2\text{CN(Me)(CH}_2)_3\text{N(Me)}_2]$ by AACVD method at 300 °C.

SEM images of the films deposited at 400 °C showed spherical nanoparticles of around 100 nm size merging with each other to form rod shaped structures (Figure 3-11). The films appear to be much smoother with even distribution of crystallites unlike to those deposited at 300 °C.

Figure 3-11: SEM images (a, b with different magnification) of silver sulfide deposited from $[\text{AgS}_2\text{CN(Me)(CH}_2)_3\text{N(Me)}_2]$ by AACVD method at 400 °C.

The films deposited at higher temperature of 500 °C show plate like structures. These plates are vertically and randomly stacked on the surface of the glass substrates (Figure 3-12). The films show some holes (without any deposition) and are less even
as compared to those deposited at 400 °C. The deposition temperature as usual has shown a clear relationship to the morphology of the films.

Figure 3-12: SEM images (a, b with different magnification) of silver sulfide deposited from \([\text{AgS}_2\text{CN(Me)(CH}_2)_3\text{N(Me)}_2]\) by AACVD method at 500 °C.

3.2.1.3 AFM of the silver sulfide thin films

The AFM of the films deposited at 300 °C clearly shows the deposition of a very thin film. The height of roughness is shown as around 7 nm (Figure 3-13). This confirms what has already been observed by p-XRD and the SEM. The AFM image of the films deposited at 400 °C show much rougher surface as compared to those deposited at 300 °C. The crystallites are grown vertically on the surface of the substrate with the height of roughness is 187 nm as shown in Figure 3-14. The AFM image of the films deposited at 500 °C show a smoother morphology than the films deposited at 400 °C which is indicated by The height of roughness is 57 nm (Figure 3-15). These results confirm the results obtained by p-XRD where the highest peak intensity is observed for the films deposited at 400 °C indicating the largest size of crystallites.
Figure 3-13: (a) AFM images (2D and 3D) of films deposited at 300 °C from trimethylpropylenediaminodithiocarbamatosilver(I) and (b) Root Mean Square of height of crystallisation.

Figure 3-14: (a) AFM images (2D and 3D) of films deposited at 400 °C from trimethylpropylenediaminodithiocarbamatosilver(I) and (b) Root Mean Square of height of crystallisation.
Figure 3-15: (a) AFM images (2D and 3D) of films deposited at 500 °C from trimethylpropylenediaminodithiocarbamatosilver(I) and (b) Root Mean Square of height of crystallisation.

3.3 Nickel sulfide

The phase diagram of nickel sulfide is much more complicated than both iron and cobalt sulfides. Ni-S system has many crystalline phases and stoichiometries including: Ni$_{3+x}$S$_2$, Ni$_3$S$_2$, Ni$_4$S$_{3+x}$, Ni$_6$S$_5$, Ni$_7$S$_6$, Ni$_9$S$_8$, NiS, Ni$_3$S$_4$ and NiS$_2$.\textsuperscript{83-85} Whilst NiS and NiS$_2$ have been studied extensively, for others only limited information is available.

NiS$_2$ (Vaesite) is a $p$-type semiconductor with a band gap of 0.5 eV. It is potentially useful in: photo electrochemical solar cells,\textsuperscript{86,87} IR detectors,\textsuperscript{88} catalysts,\textsuperscript{89} and sensors.\textsuperscript{90} It is also used as a hydrodesulphurisation catalyst and as a cathode material in rechargeable lithium batteries.\textsuperscript{91} Nickel sulfide is considered as an “Achilles heel” in toughened glass, since it is responsible for glass cancer or spontaneous glass fracture.
Rhombohedral Ni$_3$S$_2$ (heazlewoodite) is yellow in colour and exhibits semimetallic properties. It has a slightly distorted body-centred cubic arrangement of sulphur with the metal atoms in some of the pseudo-tetrahedral holes. At temperature above 556 °C, it converts to Ni$_{3+x}$S$_2$, with an fcc structure. In this phase, a sub-stoichiometric number of metal atoms are randomly distributed in a cubic close packed structure of sulphur atoms with vacancies. The spinel structured Ni$_3$S$_4$ (polydymite), at higher temperatures >400 °C, decomposes into NiS and NiS$_2$. At about 350 °C and 400 bar, Ni$_3$S$_4$ is converted into a hexagonal “NiAs-type” structure.

Ni$_7$S$_6$ has been reported to exist in two polymorphic forms, at higher temperature orthorhombic and at lower ones hexagonal, the phase transformation between these two polymorphs being sluggish. The crystal structure probably changes from hexagonal through monoclinic to orthorhombic as the stoichiometry changes, from Ni$_2$S$_8$ (through Ni$_7$S$_6$) to Ni$_6$S$_5$.

NiS (millerite) has two polymorphs with unique properties. At temperatures below 620 K, NiS has rhombohedral symmetry (millerite) and at high temperature it has the “NiAs-type” structure. In the rhombohedral form, the Ni atom is surrounded by five sulphur atoms in tetragonal pyramidal coordination, while in NiAs type, each Ni is octahedrally coordinated. Rhombohedral NiS is a semimetal with temperature independent paramagnetism, whereas hexagonal NiS undergoes a first-order phase transition from a semiconducting antiferromagnetic phase to a metallic phase.

Pramanik *et al.* have prepared nickel sulfide (NiS) films by solution growth on glass films or polymer substrates and Anuar *et al.* have electrodeposited this material. In addition to the above techniques, nickel sulfide (NiS) films have been grown by successive ionic layer adsorption and reaction (SILAR), laser ablation (NiS), hydrothermal (Ni$_3$S$_2$, NiS), soft solution-processing (Ni$_3$S$_2$, NiS$_2$, Ni$_3$S$_4$) and CVD methods (NiS, NiS$_2$, Ni$_7$S$_6$). Cheon *et al.* have reported the laser-driven photochemical vapour deposition of nickel sulfide from nickel bis(isopropylxanthate). Nomura *et al.* studied the growth of NiS$_{1.03}$ from [Ni(S$_2$CNMe$_2$)$_2$] on silicon (111) substrates by low-pressure chemical vapour deposition (LPCVD). O’Brien *et al.* have reported the deposition of nickel sulfide
films from dithiocarbamate compounds of the type \([\text{Ni}(S_2\text{CNRR'})_2]\) where \(\text{RR'} = \text{Et}, \text{MeEt}, \text{Me}''\text{Bu} \text{ or Me}''\text{Hex}, \text{by AA}^{106} \text{ and LPCVD methods.}^{107} \) They also deposited NiS thin films on glass by aerosol assisted chemical vapour deposition(AACVD) using single source precursors of the type, \([(\text{Ni}(S_2\text{COR})_2)], \text{ R} = \text{C}_2\text{H}_5 \text{ or C}_3\text{H}_7).^{109} \) The metal alkyl xanthate compounds, \(\text{M}(S_2\text{COCHR})_2, \text{ M} = \text{Ni and R} = \text{ethyl or isopropyl}
were prepared by stoichiometric reaction of potassium alkyl xanthate and metal salts following the literature method $^{110-112}$ which involved the reaction of an aqueous solution of the corresponding metal salt with the potassium xanthate aqueous solution. The metal xanthate forms rapidly and precipitates. The thermogravimetric analyses, of \([\text{Ni}(\text{C}_2\text{H}_5\text{OCS}_2)_2]\) was carried out between 25-500 °C at 10 °C min$^{-1}$ under N$_2$. \([\text{Ni}(\text{C}_2\text{H}_5\text{OCS}_2)_2]\) shows a rapid mass loss of 67 % at 155- 200 °C. The \(\text{Ni}(\text{C}_3\text{H}_7\text{OCS}_2)_2\) grown under similar conditions showed a 71% mass loss between ca. 167-202 °C. Single-step decomposition was observed for both compounds. Thin films of NiS were deposited from \([\text{Ni}(\text{C}_2\text{H}_5\text{OCS}_2)_2]\) at 200 °C, 250 °C and 300 °C. SEM studies show that the morphology of the films change with temperature. At 200 °C NiS films with rod-like morphologies are observed. These structures are approximately 500 nm in length and 250 nm in breadth, with uniform coverage on the substrate. At 250 °C the films have a twinned cube shape with interpenetrating structures. This shape is very uniform across the substrate with particles sized from 400-500 nm. There is a further change of morphology at 300 °C, where granular close-to spherical particles are observed. The coverage is non-uniform with clustered growth predominant on the substrate.

Growth from \([\text{Ni}(\text{C}_3\text{H}_7\text{OCS}_2)_2]\) at 200 °C differs from ethyl xanthate, at the similar temperature.$^2$ At 200 °C and 250 °C the films deposited could be described as granular in shape similar to those grown at 250 °C from \(\text{Ni}(\text{C}_2\text{H}_5\text{OCS}_2)_2\). There is a distinct increase in grain size as the temperature of deposition is increased from 200 to 300 °C. However the films grown at 300 °C are similar to those grown from the ethyl derivative at this temperature. Clustered growth of spherical particles is predominant on the substrate. Alam et. al. have used pyridine adducts of nickel(II) xanthates as single source precursors for the deposition of nickel sulfide thin films by AACVD.$^{113}$
Recently O’Brien et al. deposited nickel sulfide thin films from nickel complexes of thiobiuret or dithiobiuret.\textsuperscript{114} Series of compounds were synthesized and their structures determined. These compounds were used as single source precursor for deposition of nickel sulfide thin films at relatively low temperature by AACVD. In continuation of this work, \textit{bis}(trimethylethylene/propylenediaminodithiocarbamato)nickel(II) complexes were synthesized and used as single source precursors to deposit nickel sulfide thin films by AACVD method.

3.3.1 TGA of \textit{bis}(trimethylethylene-/propylenediaminodithiocarbamato)-nickel(II).

Both \textit{bis}(trimethylendiaminodithiocarbamato)nickel(II) and \textit{bis}(trimethylpropylenediaminodithiocarbamato)nickel(II) decomposed in a single major step. The ethylene derivative decomposed at about 20-30 °C lower than the propylene derivative. Also it shows a small step (10 \%) decomposition around 150 °C which is absent in the propylene derivative. The final residue for [Ni(S\textsubscript{2}CN(Me)(CH\textsubscript{2})\textsubscript{2}N(Me)\textsubscript{2})\textsubscript{2}] is about 22 \% which is the same as the calculated value. The final residue for Ni(S\textsubscript{2}CN(Me)(CH\textsubscript{2})\textsubscript{3}N(Me)\textsubscript{2})\textsubscript{2}] is about 18 \% which corresponds to the calculated value 20.6\% for nickel sulfide.

![TGA diagram](image)

Figure 3-16: TGA diagram of (a) [Ni(S\textsubscript{2}CN(Me)(CH\textsubscript{2})\textsubscript{2}N(Me)\textsubscript{2})\textsubscript{2}] and (b) Ni(S\textsubscript{2}CN(Me)(CH\textsubscript{2})\textsubscript{3}N(Me)\textsubscript{2})\textsubscript{2}].
3.3.2 Deposition of nickel sulfide thin films by AACVD method from [Ni(S$_2$CN(Me)(CH$_2$)$_2$N(Me)$_2$)$_2$]

Bis(trimethylethlenediaminedithiocarbamato)nickel(II) was prepared as described in the experimental chapter 5. Both complexes, ethylene and propylene derivatives are air and moisture stable over periods of several weeks. The complexes were soluble in toluene and THF. Before the use of complexes for deposition, both were characterised by thermal analysis. Equation 2-2.

3.3.2.1 p-XRD of nickel sulfide thin films

The p-XRD pattern of the films deposited at 300 °C showed comparatively broad bands with low intensity whereas the films deposited at 400 °C and 500 °C showed sharper bands with higher intensity indicating the growth of larger crystallites at higher temperatures. At all temperatures the peaks correspond to a mixture of orthorhombic Ni$_7$S$_6$ (ICDD card No. 00-024-1021) and (green) hexagonal NiS$_{1.03}$ (ICDD card No. 00-002-1273) with dominant phase being NiS$_{1.03}$ (Figure 3-17).

![XRD diagram of films deposited by AACVD from [Ni(S$_2$CN(Me)(CH$_2$)$_2$N(Me)$_2$)$_2$] at 300 °C, 400 °C, and 500 °C. Peaks indexed to mixture of orthorhombic Ni$_7$S$_6$ (ICDD card No. 00-024-1021) and (green) hexagonal NiS$_{1.03}$ (ICDD card No. 00-002-1273).](image-url)
Nomura et al. deposited NiS$_{1.03}$ from [Ni(S$_2$CNEt$_2$)$_2$] on silicon (111) substrates by low-pressure chemical vapour deposition (LPCVD), and O’Brien et al. have reported the deposition of nickel sulfide films from dithiocarbamate compounds of the type [Ni(S$_2$CNRR’)$_2$] where RR’ = Et$_2$, MeEt, Me”Bu or Me”Hex, by AACVD and LPCVD methods. They also deposited NiS thin films on glass by AACVD, using single source precursors of the type, ([Ni(S$_2$COR)$_2$], R = C$_2$H$_5$ or C$_3$H$_7$). The thin films deposited in this work show a mixture of Ni$_7$S$_6$ and NiS$_{1.03}$ with the NiS$_{1.03}$ being the dominant phase. The difference is the presence of Ni$_7$S$_6$ phase in our deposited films.

3.3.2.2 SEM of nickel sulfide thin films deposited by AACVD from [Ni(S$_2$CN(Me)(CH$_2$)$_2$N(Me)$_2$)$_2$]

The SEM images of the films deposited at 300 °C showed a network of spider webs. The threads appear to be several microns long.

Figure 3-18: SEM images (a, b with different magnification) of nickel sulfide deposited from [Ni(S$_2$CN(Me)(CH$_2$)$_2$N(Me)$_2$)$_2$] by AACVD method at 300 °C.

Figure 3-19: SEM images (a, b with different magnification) of nickel sulfide deposited from [Ni(S$_2$CN(Me)(CH$_2$)$_2$N(Me)$_2$)$_2$] by AACVD method at 400 °C.
These structures are completely different than those reported by O’Brien et al.\textsuperscript{114} which show the growth of network of tubular structures.

The spider web structure change to feather like structures when the deposition temperature was increased to 400 °C (Figure 3-19). The morphology of the films drastically changes when the deposition temperature is increased even further to 500 °C. The SEM images of the films deposited at 500 °C show the growth of thick clusters of plate like crystallites with some structures like sticks (Figure 3-20).

Figure 3-20: SEM images (a, b with different magnification) of nickel sulfide deposited from [Ni(S\textsubscript{2}CN(Me)(CH\textsubscript{2})\textsubscript{2}N(Me)\textsubscript{2})\textsubscript{2}] by AACVD method at 500 °C.

The effect of deposition temperature is always significant as observed in this case on the morphology of the films.

\textbf{3.3.2.3 AFM of the nickel sulfide thin films}

The AFM of the films deposited at 300 °C, 400 °C, 500 °C are shown in Figure 3-21, Figure 3-22 and Figure 3-23 respectively. Three clearly different surface morphologies are shown by these figures. There is a massive height of roughness of the surface (2.3 µm) for the films deposited at 300 °C. The films deposited at 400 °C and 500 °C show similar height of roughness of the surface (300 nm) which is considerably smaller than those deposited at 300 °C.
Figure 3-21: (a) AFM images (2D and 3D) of films deposited at 300 °C from \textit{bis}(trimethylethylenediaminodithiocarbamato)nickel(II) and (b) Root Mean Square of height of crystallisation.
Figure 3-22: (a) AFM images (2D and 3D) of films deposited at 400 °C from bis(trimethylethylenediaminodithiocarbamato)nickel(II) and (b) Root Mean Square of height of crystallisation.
Figure 3-23: (a) AFM images (2D and 3D) of films deposited at 500 °C from bis(trimethylethylenediaminodithiocarbamato)nickel(II) and (b) Root Mean Square of height of crystallisation.

3.3.2.4 p-XRD pattern of nickel sulfide thin films deposited from Ni(S₂CN(Me)(CH₂)₂N(Me))₂]

The p-XRD pattern of the films deposited at 300 °C showed a broad hump around 2-theta 20 which indicate that the films were either too thin to give any pattern or the deposited material is amorphous. The films deposited at 400 °C and 500 °C showed sharper bands with higher intensity indicating the growth of larger crystallites at higher temperatures. The p-XRD patterns peaks obtained for thin films deposited at 400 °C and 500 °C correspond to a mixture of orthorhombic Ni₇S₆ (ICDD card No. 00-024-1021) and (green) hexagonal NiS₁.₀₃ (ICDD card No. 00-002-1273) with dominant phase being NiS₁.₀₃ (Figure 3-24).
Figure 3-24: p-XRD pattern of films deposited by AACVD from [Ni(S$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$)$_2$] at 300 °C, 400 °C, and 500 °C. Peaks indexed to mixture of orthorhombic Ni$_7$S$_6$ (ICDD card No. 00-024-1021), and (green) hexagonal NiS$_{1.03}$ (ICDD card No. 00-002-1273).

The results are similar to those deposited from Ni(S$_2$CN(Me)(CH$_2$)$_2$N(Me)$_2$)$_2$] except than very thin deposition occurred at 300 °C and also to those reported by Nomura et. al. and O’Brien et. al. 105 and 107,109

3.3.2.5 SEM of nickel sulfide thin films from [Ni(S$_2$CN(Me)(CH$_2$)$_2$N(Me)$_2$)$_2$]

The SEM images of the films deposited at 300 °C showed the random shaped crystals thinly distributed over the surface of the glass substrate. This thin distribution of the crystals on the surface of the substrate was the reason for the absence of diffraction peaks in the p-XRD pattern. The shape of these crystals ranges from spherical to hexagonal to tubular and the size ranges from 5 µm to over 10 µm. It appears that the smaller crystallites join together to form large structures (Figure 3-25). The shape and size hence the morphology of these films is different to that observed for those deposited from [Ni(S$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$)$_2$] or reported by O’Brien et. al. 114
Figure 3-25: SEM images (a, b with different magnification) of nickel sulfide deposited from \([\text{Ni(S}_2\text{CN(Me)(CH}_3\text{)}_3\text{N(Me)}_2\text{)}_2]\) by AACVD method at 300 °C.

A considerable change in the morphology of the films is observed at the deposition temperature of 400 °C (Figure 3-26). The thin flakes join together to make a bunch or long tubular structures. Also unlike the films deposited at 300 °C, the surface appears to be densely packed.

Figure 3-26: SEM images (a, b with different magnification) of nickel sulfide deposited from \([\text{Ni(S}_2\text{CN(Me)(CH}_3\text{)}_3\text{N(Me)}_2\text{)}_2]\) by AACVD method at 400 °C.
Figure 3-27: SEM images (a, b with different magnification) of nickel sulfide deposited from \([\text{Ni(S}_2\text{CN(Me)(CH}_2\text{)}_2\text{N(Me)}_2\text{)}_2]\) by AACVD method at 500 °C.

The films deposited at higher temperature of 500 °C appear to be composed of flower like crystallites which are made by the cluster of plates (Figure 3-27). The surface is densely packed with these crystals. The sharp peaks in the p-XRD pattern for the films deposited at 400 °C or 500 °C confirm the observation by SEM.

3.3.2.6 **AFM of the nickel sulfide thin films from Ni(S\_2CN(Me)(CH\_2\_3N(Me)\_2))\_2**

The AFM show the morphology of the films deposited at 300 °C (Figure 3-28). Crystals of random shapes are thinly laid on the surface of the substrate. The height of roughness of the surface is 652 nm. The AFM of films deposited at 400 °C show the surface covered by flake like structures (Figure 3-29). The height of roughness of the surface is considerably smaller than those deposited at 300 °C.
Figure 3-28: (a) AFM images (2D and 3D) of films deposited at 300 °C from bis(trimethylpropylenediaminodithiocarbamato)nickel(II) and (b) Root Mean Square of height of crystallisation.

AFM of the films deposited at 500 °C showed a similar uneven surface covered with some large lumps of plates with the height of roughness (162 nm) close to those deposited at 400 °C (Figure 3-30).
Figure 3-29: (a) AFM images (2D and 3D) of films deposited at 400 °C from bis(trimethylpropylenediaminodithiocarbamato)nickel(II) and (b) Root Mean Square of height of crystallisation.
Figure 3-30: (a) AFM images (2D and 3D) of films deposited at 500 °C from bis(trimethylpropylenediaminodithiocarbamato)nickel(II) and (b) Root Mean Square of height of crystallisation.

3.4 Cobalt sulfide
Magnetic semiconductors especially cobalt sulfide, have attracted considerable attention in recent years in solar energy absorptions,\textsuperscript{115} ultra- high density magnetic recording,\textsuperscript{116} anodes for Li-ion batteries,\textsuperscript{117} and hydrodesulphurization and dehydrodearomatization.\textsuperscript{118,119} Cobalt sulfide usually exists in the form of different crystalline phases and stoichiometries including:

\text{Co}_4\text{S}_3, \text{Co}_9\text{S}_8, \text{CoS}, \text{Co}_{1-X}\text{S}, \text{Co}_3\text{S}_4, \text{Co}_2\text{S}_3, \text{and CoS}_2.\textsuperscript{120,121}
Cobalt sulfide thin films have been prepared by various methods such as chemical bath deposition (CBD), chemical vapour deposition (CVD), electrochemical deposition (ECD), and Langmuir-Blodgett (LB) methods. O’Brien et. al. used methyl n-hexyl derivatives of dithiocarbamates [Co(S₂CNMe₉Hex)₃] of cobalt as single source precursor for the growth of cobalt sulfide films and reported the deposition of Co₁₋ₓS, CoS₂ and Co₃S₄. They also synthesised several cobalt(III) complexes of 1,1,5,5-tetramethyl[Co{N(SCNMe₂)}₃] and 1,1,5,5-tetraethyl -2,3-dithibiuret [Co{N(SCNEt₂)}₃] to deposit phase selective cobalt monosulfide (Co₁₋ₓS) thin films by AACVD method and nanoparticles by colloidal preparation. The X-ray diffraction (XRD) of the deposited films showed deposition of hexagonal cobalt monosulfide. The morphology of films characterised by SEM shows rod like crystallites. The films deposited at 350 °C were sulphur deficient whereas the deposition at higher temperature showed the ratio of Co:S closer to 1:1. TEM of the samples obtained from thin films showed that the films are composed of hexagonal nanoplates.

3.4.1 TGA of [Co(S₂CN(Me)(CH₂)₂N(Me)₂)₃] and [Co(S₂CN(Me)(CH₂)₂N(Me)₂)₃].

The TGA of tris(trimethylethylenediaminedithiocarbamato)cobalt(III) and tris(trimethylpropylenediaminedithiocarbamato)cobalt(III) are shown in Figure 3-31. Both compounds decompose sharply around 250 °C into a single step to give around 12 % residue which is close to the calculated values 15% and 14% respectively for cobalt sulfide.
3.4.2 Deposition of cobalt sulfide by AACVD method

[Co(S₂CN(Me)(CH₂)₂N(Me)₂)₃].

The cobalt complex was prepared by the method described in chapter 5. Equation 2-2. Repeated attempts to recrystallise the compound to get good enough quality crystals for X-ray were unsuccessful. The solid compound is soluble in toluene and THF for AACVD.

3.4.2.1 p-XRD of cobalt sulfide thin films

The p-XRD pattern of the films deposited at 300 °C showed the peaks corresponding to a mixture of cubic Co₃S₄ (ICDD card No. 00-011-0121) and (green) hexagonal beta CoS₁.₀₉₇ (ICDD card No. 00-019-0366). The films deposited at 400 °C and 500 °C showed comparatively sharper bands corresponding to only hexagonal beta CoS₁.₀₉₇ phase (ICDD card No. 00-019-0366) (Figure 3-32).
Figure 3-32: p-XRD pattern of films deposited by AACVD from [Co(S₂CN(Me)(CH₂)₂N(Me)₂)] at 300 °C, 400 °C, and 500 °C. Peaks indexed to mixture of cubic Co₃S₄ (ICDD card No. 00-011-0121) and (green) hexagonal beta CoS₁.₀₉₇ (ICDD card No. 00-019-0366).

### 3.4.2.2 SEM of cobalt sulfide thin films

Figure 3-33 shows the SEM images of the cobalt sulfide films deposited at 300 °C from [Co(S₂CN(Me)(CH₂)₂N(Me)₂)] by AACVD. The films comprise of random thick crystallites ranging from 2 to 4 µm in size. There are clear gaps in the films. The films grown at higher temperature of 400 °C show clusters of flower like structures (Figure 3-34). High resolution image (Figure 3-34(b)) of these films show a spongy structure formed by the network of plate like crystallites.
Figure 3-33: SEM images (a, b with different magnification) of cobalt sulfide deposited from [Co(S₂CN(Me)(CH₂)₂N(Me)₂)₃] by AACVD method at 300 °C.

Figure 3-34: SEM images (a, b with different magnification) of cobalt sulfide deposited from [Co(S₂CN(Me)(CH₂)₂N(Me)₂)₃] by AACVD method at 400 °C.

The films deposited at 500 °C show an even surface (Figure 3-35). It appears that the crystallites with the size of \(ca\) 20 nm formed clusters ranging from 100 nm to 500 nm. The size of these clusters is much smaller than those deposited at lower temperatures. Also the shape of these clusters is close to spherical.
Figure 3-35: SEM images (a, b with different magnification) of cobalt sulfide deposited from [Co(S$_2$CN(Me)(CH$_2$)$_2$N(Me)$_2$)$_3$] by AACVD method at 500 °C.

3.4.2.3 AFM of the cobalt sulfide thin films deposited by AACVD from [Co(S$_2$CN(Me)(CH$_2$)$_2$N(Me)$_2$)$_3$]

AFM of cobalt sulfide thin films deposited at different temperatures are shown in Figure 3-36 to Figure 3-38. The surface of the films deposited at all three temperatures (300, 400 & 500 °C) looks very similar to each other. But the height of roughness of the films is different. Those deposited at 300 °C and 400 °C show the height of roughness are 797 and 769 respectively whereas those deposited at 500 °C show the height of roughness of the surface as 1330 nm. Although the SEM images of the films deposited at 500 °C show a much smoother surface as compared to those deposited at lower temperatures but the thickness of the films deposited at 500 °C is twice as much as the others. The height of roughness of the surface for films deposited at 300 or 400 °C is almost the same.
Figure 3-36: (a) AFM images (2D and 3D) of films deposited at 300 °C from tris(trimethylethylenediaminodithiocarbamato)cobalt(III) and (b) Root Mean Square of height of crystallisation.
Figure 3-37:  (a) AFM images (2D and 3D) of films deposited at 400 °C from \textit{tris}(trimethylethlenediaminodithiocarbamato)cobalt(III) and (b) Root Mean Square of height of crystallisation
Figure 3-38: (a) AFM images (2D and 3D) of films deposited at 500 °C from trsi(trimethylethlyenediaminodithiocarbamato)cobalt(III) and (b) Root Mean Square of height of crystallisation.

3.4.2.4 p-XRD of cobalt sulfide thin films deposited by AACVD from [Co(S₂CN(Me)(CH₂)₃N(Me)₂)₃].

The p-XRD patterns of cobalt sulfide thin films deposited from [Co(S₂CN(Me)(CH₂)₃N(Me)₂)₃] at 300, 400 and 500 °C are given in Figure 3-39. The pattern obtained for the films deposited at 300 °C show a broad hump between 20 to 30 2theta and very low intensity bands corresponding to hexagonal beta CoS₁₀₉₇ (ICDD card No.00-019-0366). Those deposited at 400 °C show a similar broad hump but comparatively stronger peaks corresponding to cubic Co₃S₄ (ICDD card no. 04-007-1256) whereas the films deposited at 500 °C show a pattern of peaks which are indexed to a mixture of hexagonal beta CoS₆₉ (ICDD card No.00-019-0366) and (green) and cubic Co₆S₈ (ICDD card no. 00-003-0631).
Figure 3-39: XRD diagram of films deposited by AACVD from \([\text{Co(S}_2\text{CN(Me)(CH}_2\text{)}_2\text{N(Me)}_2\text{)}_3]\) at 300, 400 and 500 °C. At 300 °C Peaks are indexed to hexagonal beta CoS\textsubscript{1.097} (ICDD card No.00-019-0366). At 400 °C the peaks are indexed to cubic Co\textsubscript{3}S\textsubscript{4} (ICDD card no. 04-007-1256) and at 500 °C the peaks are indexed to mixture of hexagonal beta CoS\textsubscript{1.097} (ICDD card No.00-019-0366) and (green) cubic Co\textsubscript{9}S\textsubscript{8} (ICDD card no. 00-003-0631).

The complex \([\text{Co(S}_2\text{CN(Me)(CH}_2\text{)}_2\text{N(Me)}_2\text{)}_3]\) produced mixed phases of cobalt sulfide at lower deposition temperature of 300 °C and gave pure phase (Figure 3-32) of cobalt sulfide at higher deposition temperatures of 400 °C and 500 °C, whereas the complex \([\text{Co(S}_2\text{CN(Me)(CH}_2\text{)}_3\text{N(Me)}_2\text{)}_3]\) showed opposite results and gave pure phase of cobalt sulfide at lower deposition temperatures of 300 °C and 400 °C and produced
mixed phases of cobalt sulphide at higher deposition temperature of 500 °C (Figure 3-39).

3.4.2.5 SEM of cobalt sulfide thin films from [Co(S₂CN(Me)(CH₂)₃N(Me)₂)₃]

The SEM images of the films deposited at three different temperatures (300, 400 and 500 °C) show three distinct morphologies (Figure 3-40, Figure 3-41 and Figure 3-42). The films deposited at 300 °C show granular crystallites unevenly distributed on the surface of the glass substrate. The size of these crystallites ranges from 200-300 nm.

![SEM images (a, b with different magnification) of cobalt sulfide deposited from [Co(S₂CN(Me)(CH₂)₃N(Me)₂)₃] by AACVD method at 300 °C.](image)

The films deposited at 400 °C show the growth of branched crystals which are densely packed on the surface of the substrate. The size of these branches ranges from about 200 to 600 nm (Figure 3-41). Those deposited at 500 °C show the growth of rods and plates with some other random shapes which are very densely packed. The size of these crystals varied from 1µm to 2 µm long and approx. 100 nm to 500 nm thick (Figure 3-42).
Figure 3-41:  SEM images (a, b with different magnification) of cobalt sulfide deposited from $[\text{Co(S}_2\text{CN(Me)(CH}_2\text{)}_3\text{N(Me)}_2\text{)}_3]$ by AACVD method at 400 °C.

Figure 3-42:  SEM images (a, b with different magnification) of cobalt sulfide deposited from $[\text{Co(S}_2\text{CN(Me)(CH}_2\text{)}_3\text{N(Me)}_2\text{)}_3]$ by AACVD method at 500 °C.

3.4.2.6 AFM of the cobalt sulfide thin film from bis(trimethylpropylenediaminodithiocarbamato)cobalt(III)

The AFM of the films deposited at 300 °C show a very thin deposition with random shaped crystals thinly scattered over the surface of substrate (Figure 3-43).
Figure 3-43: (a) AFM images (2D and 3D) of films deposited at 300 °C from tris(trimethylpropylenediaminodithiocarbamato)cobalt(III) and (b) Root Mean Square of height of crystallisation.
The low intensity signals in the p-XRD pattern can now be explained from the AFM images. The height of roughness of the surface was observed as 156 nm.

Figure 3-44: (a) AFM images (2D and 3D) of films deposited at 400 °C from tris(trimethylpropylenediaminodithiocarbamato)cobalt(III) and (b) Root Mean Square of height of crystallisation.
Comparatively thicker films were grown at 400 or 500 °C. The AFM images show that films grown at 400 °C are dense but with highly uneven surface which was clear from the height of roughness of the surface (661 nm).

Figure 3-45: (a) AFM images (2D and 3D) of films deposited at 500 °C from tris(trimethylpropylenediaminodithiocarbamato)cobalt(III) and (b) Root Mean Square of height of crystallisation.

The images for the films grown at 500 °C show more densely packed surface but with even greater roughness of the surface. The height of roughness of the surface was found to be 1.54 μm which is considerably larger than those deposited at 300 or 400 °C.
3.5 Conclusion

All four trimethylpropylenediaminodithiocarbamatometal complexes decompose in a clean single step. The p-XRD pattern of the copper sulfide films deposited at all temperatures show the deposition of polycrystalline films of a mixture of tetragonal \( \text{Cu}_2\text{S} \) and rhombohedral \( \text{Cu}_6\text{S}_5 \) whereas the peaks in the p-XRD patterns of silver sulfide thin films deposited at all three temperature were indexed to the monoclinic \( \text{Ag}_2\text{S} \). The p-XRD pattern of the cobalt sulfide thin films deposited at 300 °C showed the peaks corresponding to a mixture of cubic \( \text{Co}_3\text{S}_4 \) and hexagonal beta \( \text{CoS}_{1.097} \). The films deposited at 400 °C and 500 °C showed comparatively sharper bands corresponding to only hexagonal beta \( \text{CoS}_{1.097} \) phase. The deposition of nickel sulfide thin films from ethylene derivative at 300 °C showed comparatively broad bands in the XRD pattern whereas the films deposited at 400 °C and 500 °C showed sharper bands with higher intensity indicating the growth of larger crystallites at higher temperatures. At all temperatures the peaks correspond to a mixture of orthorhombic \( \text{Ni}_7\text{S}_6 \) and hexagonal \( \text{NiS}_{1.03} \) with dominant phase being \( \text{NiS}_{1.03} \). Significant differences were noted in the morphology of the thin films deposited at different temperatures.
3.6 References


Chapter 4: Deposition and characterization of indium sulfide and related ternary materials

Chapter 4 describes the X-ray structures of two new indium complexes \([\text{In}(\text{S}_2\text{CN}(\text{Me})(\text{CH}_2)_n\text{N(Me)}_2)_3]\) (\(n = 2, 3\)) and their use as precursors for the deposition of indium sulfide thin films by AACVD. The major part of this chapter is about the deposition of ternary materials including copper indium disulfide, silver indium disulfide and cadmium zinc sulfide from using the combination of copper and indium, silver and indium and zinc and cadmium precursors respectively.
4.1 Indium sulfide

The III–VI materials are alternatives to those of II–VI series especially in photovoltaic applications. However, their polytypism and the variety of stoichiometries are a problem as compared to the II–VI materials and the availability of some of the elements notably indium, is somewhat limited. Among III–VI semiconductors, indium sulfide is investigated due to its interesting properties in relation to the production of photovoltaic and optoelectronic devices. In$_2$S$_3$ is a n-type semiconductor with a wide energy band gap (2.0–2.8 eV) and is a non-toxic material. Owing to its stability, optical, optoelectronic, and electronic properties it can find many applications, such as luminophors, solar cell devices, optoelectronic, and heterojunction for use in photovoltaic electric generators, buffer layers in CIGS-type solar cells, electrodes for photochemical solar cells, inorganic–organic solar cells, green and red phosphors for television picture tubes, or the photocatalytic production of hydrogen.

The structure of indium sulfide can be derived from a II–VI compound in which the divalent metal is replaced by trivalent indium, leading to a cubic or hexagonal close-packed structure of non-metal atoms in which a part (one third) of the cation sites remain empty in order to preserve the electroneutrality. This defect structure allows three modifications, namely a cubic (disordered spinel-type), a tetragonal (ordered spineltype) and a trigonal structure, which are generally referred to as $\alpha$, $\beta$ and $\gamma$ polymorphs. The $\beta$-In$_2$S$_3$ phase is stable below 420 °C.

In$_2$S$_3$ films exhibit significant differences in their structural, optical, chemical and electrical properties depending on the reported thin film deposition conditions. Various techniques are used, such as chemical vapour deposition, physical vacuum deposition, atomic layer epitaxy, successive ionic layer adsorption and reaction (SILAR), spray pyrolysis, and chemical bath deposition (CBD) and Modulated flux deposition (MFD).

Several single source precursors have been used to prepare indium sulfide thin films or nanoparticles. Nomura et. al. successfully prepared dimeric volatile alkylindium
alkyl thiolates by introducing steric bulk both at the alkyl and to the thiolate. These compounds are typically liquids at room temperature and can be distilled under reduced pressure (> 10^{-3} Torr). The deposition of the two different types of indium sulfide was controlled by the number of thiolate ligands bound to the indium atom; dialkyindium monothiolates give InS and monoalkylindium dithiolates produce β-In$_2$S$_3$ at 300 °C under static pyrolysis conditions. Nomura's group used $^n$Bu$_2$In(S'SPr), as a source for indium sulfide deposition and highly orientated films of β-In$_2$S$_3$ with a strongly preferred (103) growth direction were deposited on Si(111) or quartz substrates at temperatures in the range 300-400 °C. Orthorhombic InS films could be deposited at lower temperatures using Bu$_2$In(SPr) as a source, but the presence of trace amounts of oxygen in the carrier gas caused the partial oxidation of the InS layers leading to highly conductive films of indium oxide doped with sulphur at 275°C. In related work the dimeric indium thiolate [tBuIn(μ-S$t^3$Bu)$_2$] was used to deposit a polycrystalline, tetragonal high-pressure form of β-In$_2$S$_3$. Films of indium sulfide have been grown from dimethyl-, diethyl-, or dineopentylindium diethylidithiocarbamates ([R$_2$InS$_2$CNEt$_2$] with R = Me, Et, or Np), which are air-sensitive compounds. The films were grown on (100)-GaAs substrates, using a cold-wall, low-pressure reactor. The methyl complex deposits orthorhombic InS and monoclinic In$_6$S$_7$ phases between 425 and 400 °C, whereas growth at 325 °C results in cubic β-In$_2$S$_3$. In contrast, the ethyl compound deposits monophasic, crystalline β-In$_2$S$_3$ over the range 350-400 °C. These results show the role played by the change of alkyl groups. They suggest that the amount of carbon incorporation, which relates to the β-H elimination process, may well influence the film's composition.

Tris-complexes of indium [In(E$_2$CNMeR)$_3$] have been used in experiments, where E = S with R = $^n$butyl or $^n$hexyl, and E = Se with R = $^n$hexyl. In$_2$S$_3$ films were grown from [In(S$_2$CNMe$n$Bu)$_3$] or [In(S$_2$CNMe$n$Hex)$_3$], at 450 - 500 °C temperature onto glass, GaAs, or InP by LP-MOCVD. Cubic α-In$_2$Se$_3$ was the predominant phase, sometimes, mixed with some hexagonal β-In$_2$Se$_3$ phase when the n-butyl derivative was used. The deposition of predominately α-In$_2$Se$_3$, regardless of growth conditions, shows a clean gas phase decomposition process. In$_2$S$_3$ nanorods with average
diameter of 20 nm and 400-500 nm length were prepared for the first time on glass substrates from a single-source precursor, [Et₂InS₂CNMe₈Bu] by AACVD at 375 °C without either template or catalyst.³⁸

[In(S₂CO’Pr)₃] is a volatile complex from which thin films of cubic α-In₂S₃ could be grown at temperatures as low as 210 °C. Films deposited on glass were (111)-orientated.³⁹ These results are interesting with regard to the deposition of the related ternary CuInS₂ and CuInSe₂ using complexes of the type [M(E₂CNMe[R])ₙ], where R = °Bu and °Hex; M = Cu (n = 2) and M = In (n = 3).⁴⁰

Thin films of In₂S₃ have been produced from [In(SOCNET₂)]⁴¹ and [In(SOCN’Pr₂)]⁴² on glass substrates, by LP-MOCVD. [In(SOCN’Pr₂)] proved both more volatile and more efficient for film delivery than [In(SOCNET₂)]. The former led to the tetragonal β-phase at temperatures as low as 350 °C, and the latter to the cubic β-phase at 400 °C and above. Hampden-Smith and co-workers have used the facile elimination of thioacetic anhydride from polyether adducts of group 2 metal thioacetates to deposit high-purity, stoichiometric metal sulfides⁴³ and applied it to adducts of gallium and indium thioacetates.⁴⁴

4.1.1 Synthesis and X-ray structures of [In(S₂CN(Me)(CH₂)₂N(Me)₂)₃] and [In(S₂CN(Me)(CH₂)₃N(Me)₂)₃]

*Tris*(trimethyleneaminodithiocarbamato)indium(III) and *tris*(trimethylpropyleneaminodithiocarbamato)indium(III) were synthesized as described in the experimental section (chapter 5). Equation 2-2. Both complexes were crystalline solids, soluble in most organic solvents, and stable at room temperature in open atmosphere for periods of months. The molecular structure of both complexes was determined by X-ray Crystallography.

The molecular structure of *tris*(trimethyleneaminodithiocarbamato)-indium(III) is shown in Figure 4-1 and the crystallographic refinement data is given in Table 4-1. The structure is based on a monomer in which indium atom is coordinated to six sulphur atoms of three chelating thio carbamato ligands. The six sulfur atoms from three chelating dithiocarbamato ligands are arranged in a distorted octahedral
environment around the central metal atom. There is no significant difference in all six In-S bond distances (2.59 to 2.61 Å) and are similar to those reported previously.\textsuperscript{36,41,42}

Figure 4-1: Molecular structure of \([\text{In(S}_2\text{CN(Me)(CH}_2\text{)N(Me)}_2)]\). Important bond lengths (Å) and angles (°): In(1)-S(1)#1 = 2.5913(8), In(1)-S(1) = 2.5913(8), In(1)-S(1)#2 = 2.5913(8), In(1)-S(2)#2 = 2.6133(9), In(1)-S(2)#1 = 2.6134(9), In(1)-S(2) = 2.6135(9), C(1)-N(1) = 1.324(4), C(1)-S(2) = 1.725(3), C(1)-S(1) = 1.730(3); S(1)#1-In(1)-S(1) = 96.97(3), S(1)#1-In(1)-S(1)#2 = 96.97(3), S(1)-In(1)-S(1)#2 = 96.97(3), S(1)#1-In(1)-S(2)#2 = 153.83(3), S(1)-In(1)-S(2)#2 = 106.66(3), S(1)#2-In(1)-S(2)#2 = 69.55(3), S(1)#1-In(1)-S(2)#1 = 69.55(3), S(1)-In(1)-S(2)#1 = 153.82(3), S(1)#2-In(1)-S(2)#1 = 106.66(3), S(2)#2-In(1)-S(2)#1 = 92.29(3), S(1)#1-In(1)-S(2) = 106.66(3), S(1)-In(1)-S(2) = 69.55(3), S(1)#2-In(1)-S(2) = 153.83(3), S(2)#2-In(1)-S(2) = 92.29(3), S(2)#1-In(1)-S(2) = 92.29(3)

The C-S distances are also similar (close to 1.72 Å) within experimental error in the two molecules, indicating delocalization in the CS\textsubscript{2} skeleton.
Figure 4-2: Molecular structure of $\text{[In(CS}_2\text{N(Me)}(\text{CH}_2)_2\text{N(Me)}_2)]}$.  

Important bond lengths (Å) and angles (°): $\text{In(1)-S(5)} = 2.5681(11)$, $\text{In(1)-S(1)} = 2.5747(12)$, $\text{In(1)-S(4)} = 2.5864(12)$, $\text{In(1)-S(3)} = 2.6023(12)$, $\text{In(1)-S(2)} = 2.6047(12)$, $\text{In(1)-S(6)} = 2.6075(12)$, $\text{C(1)-N(1)} = 1.323(5)$, $\text{C(1)-S(2)} = 1.727(5)$, $\text{C(1)-S(1)} = 1.732(4)$; $\text{S(5)-In(1)-S(1)) = 94.94(4)$, $\text{S(5)-In(1)-S(4)) = 101.87(4)$, $\text{S(5)-In(1)-S(3)) = 159.01(4)$, $\text{S(5)-In(1)-S(2)) = 98.03(4)$, $\text{S(1)-In(1)-S(3)) = 95.66(4)$, $\text{S(5)-In(1)-S(2)) = 69.79(4)$, $\text{S(5)-In(1)-S(2)) = 158.89(4)$, $\text{S(1)-In(1)-S(2)) = 70.06(4)$, $\text{S(5)-In(1)-S(3)) = 96.37(4)$, $\text{S(5)-In(1)-S(3)) = 98.18(4)$, $\text{S(5)-In(1)-S(2)) = 69.96(4)$, $\text{S(1)-In(1)-S(6)) = 105.08(4)$, $\text{S(4)-In(1)-S(6)) = 92.54(4)$, $\text{S(3)-In(1)-S(6)) = 156.64(4)$, $\text{S(2)-In(1)-S(6)) = 98.91(4)$
Table 4-1: Crystal data and structure refinement for \([\text{In} (\text{S}_2\text{CN(Me})(\text{CH}_2)_2\text{N(Me)}_2)_3]\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>([\text{In} (\text{S}_2\text{CN(Me})(\text{CH}_2)_2\text{N(Me)}_2)_3])</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>(\text{C}<em>{18}\text{H}</em>{39}\text{N}_6\text{S}_6\text{In})</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>646.73</td>
</tr>
<tr>
<td><strong>Crystal system, space group</strong></td>
<td>Rhombohedral, (\text{R-3})</td>
</tr>
</tbody>
</table>
| **Unit cell dimensions** | \(a = 15.6156(10)\ \text{Å}\ \alpha = 90°\)  
\(b = 15.6156(10)\ \text{Å}\ \beta = 90°\)  
\(c = 20.572(3)\ \text{Å}\ \gamma = 120°\) |
| **Volume** | 4344.3(7)\(\text{Å}^3\) |
| **Z, Calculated density** | 6, 1.483\(\text{Mg/m}^3\) |
| **Absorption coefficient** | 1.267\(\text{mm}^{-1}\) |
| **Crystal size** | 0.18 x 0.16 x 0.03 mm |
| **Theta range for data collection** | 2.49 to 28.29° |
| **Data / restraints / parameters** | 2317 / 0 / 97 |
| **Goodness-of-fit on \(F^2\)** | 0.656 |
| **Final R indices [I>2\(\sigma(I)\)]** | \(R_1 = 0.0354, \ wR_2 = 0.0594\) |
| **R indices (all data)** | \(R_1 = 0.0623, \ wR_2 = 0.0656\) |
| **Largest diff. peak and hole** | 0.719 and -0.504 e.\(\text{Å}^{-3}\) |
| **Reflections collected / unique** | 9274 / 2317 [\(R(\text{int}) = 0.0728\)] |
| **Limiting indices** | \(-20\leq h \leq 17, \ -11\leq k \leq 20, \ -26\leq l \leq 27\) |
The C-N distances, which are close to 1.32 Å, are significantly shorter than the normal single bond, suggesting considerable double bond character, as expected for metal dithiocarbamates. All three four-membered rings are close to planar. The observed distortion of the octahedral geometry is attributed to the small bite angle 69.5° of the chelating dithiocarbamato-ligand. The overall geometry of both complexes is similar to those reported for other related dithiocarbamato complexes of indium.\textsuperscript{36,41,42}

Table 4-2: Crystal data and structure refinement for [In (S$_2$CN(Me))(CH$_2$)$_3$N(Me)$_2$]$_3$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>[In (S$_2$CN(Me))(CH$_2$)$_3$N(Me)$_2$]$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{21}$H$</em>{45}$N$_6$S$_6$In</td>
</tr>
<tr>
<td>Formula weight</td>
<td>688.81</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Triclinic, P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a = 10.2335(11) Å  alpha = 82.054(2) °</td>
<td></td>
</tr>
<tr>
<td>b = 11.3421(12) Å  beta = 75.621(2) °</td>
<td></td>
</tr>
<tr>
<td>c = 14.5832(16) Å  gamma = 89.501(2) °</td>
<td></td>
</tr>
<tr>
<td>Volume</td>
<td>1623.3(3)Å$^3$</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>2, 1.409Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.135 mm$^{-1}$</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.22 x 0.19 x 0.15 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.46 to 28.28 °</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>7234 / 0 / 316</td>
</tr>
<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>0.912</td>
</tr>
<tr>
<td>Final R indices [I&gt;2σ(I)]</td>
<td>R1 = 0.0403, wR2 = 0.0817</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0567, wR2 = 0.1121</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.933 and -0.618e.A$^-3$</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>10333 / 7234 [R(int) = 0.0417]</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-12&lt;=h&lt;=13, -14&lt;=k&lt;=14, -14&lt;=l&lt;=19</td>
</tr>
</tbody>
</table>
The structure of tris(trimethylpropylenediaminedithiocarbamato)indium(III) is shown in Figure 4-2 and the crystal refinement data is given in Table 4-2. The structure of tris(trimethylpropylenediaminodithiocarbamato)indium(III) is similar to tris(trimethylethylendiaminodithiocarbamato)indium(III) with the only difference that the In-S, C-S and C-N bond distances are slightly shorter and bite angles of the thiocarbamato ligands are slightly larger in tris(trimethylpropylenediaminedithiocarbamato)indium(III).

4.1.2 TGA of [In(S₂CN(Me)(CH₂)₂N(Me)₂)₃] and [In(S₂CN(Me)(CH₂)₃N(Me)₂)₃]
The TGA of both complexes is shown in Figure 4-3. Both complexes decompose in a clean single step to give about 20% residue which correspond to indium sulfide. The calculated value for indium sulfide is 22% and 21% for [In(S₂CN(Me)(CH₂)₂N(Me)₂)₃] and [In(S₂CN(Me)(CH₂)₃N(Me)₂)₃] respectively. [In(S₂CN(Me)(CH₂)₂N(Me)₂)₃] decompose at almost 100 °C lower (190 °C) than the [In(S₂CN(Me)(CH₂)₃N(Me)₂)₃] (290 °C). This significantly large difference in decomposition temperature of these complexes is not observed in the corresponding bis complexes (see chapter 2 and 3). Indium was the only metal used with oxidation state three to prepare these complexes so we cannot be sure that this decomposition trend persist for other metals with similar oxidation states. It will be interesting to synthesise other tris complexes and compare their decomposition behaviour and draw rationale for this behaviour. As such we were unable to draw any conclusions for such a large difference in the decomposition of these two complexes. However the TGA results indicate that both compounds are potentially suitable for the AACVD deposition of indium sulfide thin films.
Figure 4-3: TGA diagram of: (a) [In(S₂CN(Me)(CH₂)₂N(Me)₂)₃] and (b) [In(S₂CN(Me)(CH₂)₃N(Me)₂)₃].

4.1.3 Deposition of indium sulfide thin films from [In(S₂CN(Me)(CH₂)₂N(Me)₂)₃] and [In(S₂CN(Me)(CH₂)₃N(Me)₂)₃] by AACVD

Both tris(trimethylethlenediaminodithiocarbamato)indium(III) and tris(trimethylpropylenediaminodithiocarbamato)indium(III) were used to deposit indium sulfide thin films onto glass substrates by AACVD method.

4.1.3.1 p-XRD of indium sulfide thin films deposited from [In(S₂CN(Me)(CH₂)₂N(Me)₂)₃]

The p-XRD pattern of the indium sulfide thin films deposited onto glass substrates from [In(S₂CN(Me)(CH₂)₂N(Me)₂)₃] by AACVD at three different temperatures of 300, 400 and 500 °C are shown in Figure 4-4. Indium sulfide deposited at 300 or 400 °C gave a broad peak between 2-theta value of 20-40 which covers the (116), (109) and (012) planes of the tetragonal In₂S₃. The broadness of the peak indicate the nanocrystal size of the deposited material or the deposition of a very thin film of indium sulfide (ICDD card No. 00-025-0390). The films deposited at higher
temperature of 500 °C show comparatively sharper peaks to correspond to other planes of the tetragonal phase of the indium sulfide. Usually but not always, the films deposited at higher temperatures result in the larger size of crystallites.

Figure 4-4: p-XRD diagram of films deposited by AACVD from \[\text{[In(S}_2\text{CN(Me)(CH}_2\text{)}_2\text{N(Me)}_2\text{)}_3\] at 300 °C, 400 °C, and 500 °C. Peaks indexed to tetragonal \text{In}_2\text{S}_3\) (ICDD card No. 00-025-0390).

4.1.3.2 SEM of indium sulfide thin films deposited from \[\text{[In(S}_2\text{CN(Me)(CH}_2\text{)}_2\text{N(Me)}_2\text{)}_3\]

SEM micrographs of the films deposited at 300 °C are shown in Figure 4-5. The morphology of the films consists of spherical particles with the size range of 300-400 nm densely packed on the surface of the substrate. The spherical nanoparticles appeared to be squashed against each other to give then distorted spherical shapes. The films deposited at 400 °C show a similar morphology to those deposited at 300 °C (Figure 4-6) but those deposited at 500 °C show a clear difference in the morphology (Figure 4-7) as was indicated by the p-XRD pattern. At the deposition temperature of 500 °C the smaller crystallites dissolve into bigger one and then form a large cluster of crystallites resulting in the sharper peaks in the p-XRD pattern.
Figure 4-5: SEM images (a, b with different magnification) of indium sulfide thin films deposited from [In(S₂CN(Me)(CH₂)₂N(Me)₂)] at 300 °C by AACVD method.

Figure 4-6: SEM images (a, b with different magnification) of indium sulfide thin films deposited from [In(S₂CN(Me)(CH₂)₂N(Me)₂)] at 400 °C by AACVD method.
4.1.3.3 **AFM of indium sulfide thin films deposited from**

\[\text{[In(S}_2\text{CN(Me)(CH}_2\text{)}_2\text{N(Me)}_2]\text{]}\]

The AFM images of the films deposited at 300, 400 and 500 °C from bis(trimethylethylenediaminodithiocarbamato) indium(III) are shown in Figure 4-8, Figure 4-9 and Figure 4-10 respectively. It was strange to note that the SEM images of the films deposited at 300 and 400 °C were similar but on the contrary the AFM images are quite different. The height of roughness of the surface for the films deposited at 300 °C was the highest (572 nm) as compared to those deposited at 400 °C (184 nm) or those deposited at 500 °C (326 nm).
Figure 4-8: (a) AFM images (2D and 3D) of films deposited at 300 °C from tris(trimethylethlenediaminodithiocarbamato)indium(III) and (b) Root Mean Square of height of crystallisation.
Figure 4-9: (a) AFM images (2D and 3D) of films deposited at 400 °C from tris(trimethylethlenediaminodithiocarbamato)indium(III) and (b) Root Mean Square of height of crystallisation.
Figure 4-10: (a) AFM images (2D and 3D) of films deposited at 500 °C from tris(trimethylethlenediaminodithiocarbamato)indium(III) and (b) Root Mean Square of height of crystallisation.
4.1.3.4 p-XRD of indium sulfide thin films deposited from [In(S$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$)$_3$]

The p-XRD patterns for the films deposited at 300, 400 and 500 °C are shown in Figure 4-11. The peaks in all three patterns are indexed to tetragonal In$_2$S$_3$ (ICDD card No. 00-025-0390). The peaks are considerably broader for the films deposited at 300 °C but the sharpness and the intensity of the peaks increases with the increase of deposition temperature. The films deposited at 500 °C show significantly sharp peaks as compared to those deposited at 300 °C. The p-XRD pattern obtained from the thin films deposited from [In(S$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$)$_3$] at all the deposition temperatures are more sharp with high intensity as compared to the p-XRD pattern of thin films deposited from [In(S$_2$CN(Me)(CH$_2$)$_2$N(Me)$_2$)$_3$].

![p-XRD diagram of films deposited by AACVD from [In(S$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$)$_3$] at 300 °C, 400 °C and 500 °C. Peaks indexed to tetragonal In$_2$S$_3$ (ICDD card No. 00-025-0390).](image)

Different phases of indium sulfide including β-In$_2$S$_3$ and In$_6$S$_7$ were deposited from mixed alkylidithiocarbamato complexes of indium by LP-CVD method. The phase
of the material was strongly dependent on the type of alkyl group in the precursor and also the deposition temperature. Bessergenev et al. have reported the deposition of α-In$_2$S$_3$ from [In(S$_2$COiPr)$_3$] by LP-MOCVD at temperatures as low as 250 °C. The same authors have presented a detailed phase analysis study of indium sulfide films grown from both this complex and [In(S$_2$CNEt$_2$)$_3$], focusing on the effects of annealing and deposition temperature by analysing the films by using synchrotron radiation diffraction.

4.1.3.5 SEM of indium sulfide thin films deposited from [In(S$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$)$_3$]

SEM Images of the films deposited at 300, 400 and 500 °C are shown in Figure 4-12,

![SEM Images](image)

Figure 4-12: SEM images (a, b with different magnification) of indium sulfide thin films deposited from [In(S$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$)$_3$] at 300 °C by AACVD method.

Figure 4-13 and Figure 4-14, respectively. SEM images for the films deposited at 300 °C show spaghetti type structures weaved into each other whereas those deposited at 400 °C show the granular crystallites forming larger clusters and those deposited at higher temperature of 500 °C show well developed irregular shaped crystals. The crystallinity appears to increase with the increase in the deposition temperature.
Figure 4-13: SEM images (a, b with different magnification) of indium sulfide thin films deposited from \([\text{In(S}_2\text{CN(Me)(CH}_2\text{)}_3\text{N(Me)}_2\text{)}_3]\) at 400 °C by AACVD method.

Figure 4-14: SEM images (a, b with different magnification) of indium sulfide thin films deposited from \([\text{In(S}_2\text{CN(Me)(CH}_2\text{)}_3\text{N(Me)}_2\text{)}_3]\) at 500 °C by AACVD method.

4.1.3.6 AFM of indium sulfide thin films deposited from \([\text{In(S}_2\text{CN(Me)(CH}_2\text{)}_3\text{N(Me)}_2\text{)}_3]\)

The AFM images of the films deposited at 300, 400 and 500 °C from \(\text{tris(trimethylpropylenediaminodithiocarbamato)indium(III)}\) are shown in Figure 4-15, Figure 4-16 and Figure 4-17 respectively. The height of roughness of the surface for the films deposited at 300 °C was again the highest (205 nm) as compared to those deposited at
400 °C (73 nm) or those deposited at 500 °C (38 nm). These roughness values are considerably smaller than those observed for films deposited from \( \text{In(S}_2\text{CN(Me)(CH}_2\text{)}_3\text{N(Me)}_2\text{)}_3 \) under similar conditions. These results show that better and even surface films were deposited from \( \text{In(S}_2\text{CN(Me)(CH}_2\text{)}_3\text{N(Me)}_2\text{)}_3 \) as compared to those deposited from \( \text{In(S}_2\text{CN(Me)(CH}_2\text{)}_2\text{N(Me)}_2\text{)}_3 \).

Figure 4-15: (a) AFM images (2D and 3D) of films deposited at 300°C from \textit{tris}(trimethylpropylenediaminodithiocarbamato)indium(III) and (b) Root Mean Square of height of crystallisation.
Figure 4-16:  (a) AFM images (2D and 3D) of films deposited at 400°C from tris(trimethylpropylenediaminodithiocarbamato)indium(III) and (b) Root Mean Square of height of crystallisation.
Figure 4-17: (a) AFM images (2D and 3D) of films deposited at 500°C from *tris*(trimethylpropylenediaminodithiocarbamato)indium(III) and (b) Root Mean Square of height of crystallisation.

### 4.2 Copper indium disulfide (CuInS₂) thin films

Semiconducting material based on multi-layered thin film composites of several elements from groups I, III and VI of the periodic table is of current interest. Combinations corresponding to the formula ABC₂ have photovoltaic effect, where A = Cu, Ag or Au, B=Al, Ga or In and C=S, Se or Te. General chalcopyrite films made
of copper, indium and sulphur/selenium are referred to by the abbreviation ‘CIS’, or ‘CIGS’ if gallium has been incorporated with the purpose of widening the band gap.

While selenium-containing CIS materials currently dominate the potential for industrial scale synthesis of chalcopyrite thin films, recent research on their sister material, CuInS$_2$, has also proved promising. The first working solar cell based on CuInS$_2$ was reported in 1977, albeit with a low efficiency of 3.3%. The major advantage of CuInS$_2$ (1.5 eV) solar cells is their inherent physical stability, while other materials suffer illumination-based degradation, exposure to light actually increases their efficiency. They have also been shown to be stable to accelerated aging conditions and possess radiation hardness.

A variety of methods has been employed for the production of CuInS$_2$ adsorber layers, most of which can be categorized as either multi-source evaporation methods or ‘2-step’ processes. The rapid thermal processing (RTP) treatment is used to deposit films on a copper tape substrate from a liquid Cu/In precursor in gaseous sulphur. Sequential methods are so named as they involve a minimum of 2 steps, namely deposition followed by sulphurization of the metal precursor films. Rapid thermal processing has taken favour here as it reduces typical annealing times from 1 h to 3 min. This method has the advantages of being fast and low cost, yet there is some doubt as to how the cells would withstand environmental impacts. The most successful of these sequences was piloted in the laboratories of the Hahn-Meitner-Institut in Germany, using RTP to heat layers of copper and indium in elemental sulphur vapour. This gave films with good crystallinity and efficiency up to 11.4%, but the process also includes lengthy latter steps including chemical bath deposition of the toxic cadmium sulfide before solar cell applications can be realised. The sulphurization process of sequential methods often also utilises the toxic H$_2$S gas.

In multi-source evaporation methods, CuInS$_2$ films are deposited on a heated substrate by evaporating the constituent elements from their respective sources. However, single source precursors are becoming increasingly popular for evaporation processes as multi-source precursors are frequently toxic, air-sensitive and pyrophoric. These ternary precursors (which can be of solid or liquid form) can be used with hot or
cold wall CVD reactors at reduced temperatures of 400-450 °C and produce films with good electrical and optical properties for photovoltaic devices.\textsuperscript{52}

The highest efficiency of selenium-free chalcopyrite films via multi-source evaporation has been achieved by incorporating gallium into CuInS\textsubscript{2} adsorber layers,\textsuperscript{53} producing solar cells with a total conversion efficiency of ≤12.3%. At higher band gaps (such as the 1.65 eV required for tandem configurations), efficiency is still greater than 10% - a significant improvement on CuInSe\textsubscript{2} based solar cells.\textsuperscript{54}

A copper excess has been found to be beneficial for the growth of CuInS\textsubscript{2} films via both sequential and evaporation methods. Excess copper cannot be incorporated into the chalcopyrite lattice\textsuperscript{55} and so instead forms a secondary phase surface layer of Cu-S. This is thought to act as a ‘flux’ with a high diffusion coefficient for species involved in the growth process, so increasing growth rates by overcoming the potential kinetic limitation of sulphur incorporation.\textsuperscript{56} Cu-rich films have been found to have larger crystallite size with less dependency on substrate temperature\textsuperscript{57} whereas Cu-poor films are poorly formed with a triangular crystallite shape.\textsuperscript{58} Park \textit{et. al.} found that varying the ratio of precursors had no specific effect on the stoichiometry of the ternary CuInS\textsubscript{2} when grown by AACVD.\textsuperscript{59} Use of AACVD as opposed to LPCVD was also found to lower the temperature required to obtain CuInS\textsubscript{2} deposition.\textsuperscript{59} CuInS\textsubscript{2} was also synthesised in our lab via AACVD from a novel combination of precursors Cu(hfac)\textsubscript{2}.H\textsubscript{2}O, and tris(diethylthiocarbamato)Indium(III), In(S\textsubscript{2}CNEt\textsubscript{2})\textsubscript{3}.

\subsection{4.2.1 Deposition of CuInS\textsubscript{2} thin films from [Cu(S\textsubscript{2}CN(Me)(CH\textsubscript{2})\textsubscript{3}N(Me)\textsubscript{2})\textsubscript{2}] and [In(S\textsubscript{2}CN(Me)(CH\textsubscript{2})\textsubscript{3}N(Me)\textsubscript{2})\textsubscript{3}]

A 1:1 stoichiometric mixture of single source precursors Cu(S\textsubscript{2}CN(Me)(CH\textsubscript{2})\textsubscript{3}N(Me)\textsubscript{2})\textsubscript{2} and [In(S\textsubscript{2}CN(Me)(CH\textsubscript{2})\textsubscript{3}N(Me)\textsubscript{2})\textsubscript{3}] was used in a THF solution to deposit CuInS\textsubscript{2} thin films onto glass substrates by AACVD method.

\subsubsection{4.2.1.1 p-XRD of CuInS\textsubscript{2} thin films deposited from [Cu(S\textsubscript{2}CN(Me)(CH\textsubscript{2})\textsubscript{3}N(Me)\textsubscript{2})\textsubscript{2}] and [In(S\textsubscript{2}CN(Me)(CH\textsubscript{2})\textsubscript{3}N(Me)\textsubscript{2})\textsubscript{3}]

The p-XRD patterns for the films deposited at 300, 400 and 500 °C are shown in Figure 4-18. The peaks in all three pattern are indexed to monoclinic Cu\textsubscript{1.701}In\textsubscript{0.05}S.
The material have very small amount of indium (0.05). The films can be described as indium doped Cu$_2$S rather than CuInS$_2$.

![Figure 4-18: p-XRD diagram of the films deposited by AACVD from Cu(S$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$)$_2$ and [In(S$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$)$_3$ at 300 °C, 400 °C and 500 °C. Peaks indexed to monoclinic Cu$_{1.701}$In$_{0.05}$S (ICDD card No. 00-045-1303).](image)

The insertion of less indium shows that either the indium precursor was less reactive at the surface of the substrate as compared to the copper precursor, or the quantity of indium precursor used was not enough to match with the required material. Given more time, I would have used larger quantity of indium precursor, as compared to copper precursor to obtain the target material.

### 4.2.1.2 SEM of copper indium sulfide thin films deposited from Cu(S$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$)$_2$ and [In(S$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$)$_3$]

SEM Images of the films deposited at 300, 400 and 500 °C are shown in Figures 4.19, 4.20, and 4.21. Irregular shaped crystallites were grown at 300 °C (Figure 4.19)
Figure 4-19: SEM images (a, b with different magnification), (c) EDAX spectrum of copper indium disulfide thin films deposited from \([\text{Cu}(\text{S}_2\text{CN}(\text{Me})(\text{CH}_2)_3\text{N(Me)}_2)_2] \) and \([\text{In}(\text{S}_2\text{CN}(\text{Me})(\text{CH}_2)_3\text{N(Me)}_2)_3] \) at 300 °C by AACVD.

Flakes were grown at 400 °C (Figure 4-20) and feather like structures at 500 °C, (Figure 4-21). Energy dispersive X-Ray spectroscopy analysis of the thin films show that the composition ratio of (Cu:In:S) is: (~ 28:35:37) (~ 1:1:1) at 300 °C (Figure 4-19), (~ 26:28:46) (~1:1:2) at 400 °C (Figure 4-20) and (~33:21:46) (~2:1:2) at 500 °C (Figure 4-21). From these results it appears that the films deposited at 400 °C give almost the right material where ratio of (Cu:In:S) is (~ 1:1:2).
Figure 4-20: SEM images (a, b with different magnification), (c) EDAX spectrum of copper indium disulfide thin films deposited from [Cu(S₂CN(Me)(CH₂)₃N(Me)₂)₂] and [In(S₂CN(Me)(CH₂)₃N(Me)₂)₃] at 400 °C by AACVD.
Figure 4-21: SEM images (a, b with different magnification), (c) EDAX spectrum of copper indium disulfide thin films deposited from \([\text{Cu(S}_2\text{CN(Me)(CH}_3\text{)}_3\text{N(Me)}_2\text{)}_2]\) and \([\text{In(S}_2\text{CN(Me)(CH}_2\text{)}_3\text{N(Me)}_2\text{)}_3]\) at 500 °C by AACVD.

4.2.1.3 AFM of copper indium sulfide thin films deposited from \([\text{Cu(S}_2\text{CN(Me)(CH}_3\text{)}_3\text{N(Me)}_2\text{)}_2]\) and \([\text{In(S}_2\text{CN(Me)(CH}_2\text{)}_3\text{N(Me)}_2\text{)}_3]\)

The AFM images of the films deposited at 300, 400 and 500 °C from \(\text{bis(trimethylpropylenediaminodithiocarbamato)copper(II)}\) and \(\text{tris(trimethylpropylene-diaminodithiocarbamato)indium(III)}\) are shown in Figure 4-22, Figure 4-23 and Figure 4-24, respectively.
Figure 4-22: (a) AFM images (2D and 3D) of films deposited at 300 °C from \textit{bis}(trimethylpropylenediaminodithiocarbamato)copper(II) and \textit{tris}(trimethylpropylenediaminodithiocarbamato)indium(III) and (b) Root Mean Square of height of crystallisation.

The height of roughness of the surface for the films deposited at 300, 400 and 500 °C was observed as 297, 116, and 691 nm respectively. Films with the largest crystallites showed the most uneven surface.
Figure 4-23: (a) AFM images (2D and 3D) of films deposited at 400 °C from \textit{bis}(trimethylpropylenediaminodithiocarbamato)copper(II) and \textit{tris}(trimethylpropylenediaminodithiocarbamato)indium(III) and (b) Root Mean Square of height of crystallisation.
Figure 4-24: (a) AFM images (2D and 3D) of films deposited at 500 °C from bis(trimethylpropylenediaminodithiocarbamato)copper(II) and tris(trimethylpropylenediaminodithiocarbamato)indium(III) and (b) Root Mean Square of height of crystallisation.

4.3 Silver indium sulfide

The I-III-VI ternary semiconductors with the chalcopyrite structure have useful applications in solar cells and optical devices. Both AgInS$_2$ and AgIn$_3$S$_8$ have the energy band gap in the range of 1.7-2.0 eV. Both can be prepared to have either n- or p-type conductivity and have a resistivity between 102 and 106 Ω-cm, depending on the method used for deposition of thin films. AgInS$_2$ has
tetragonal and orthorhombic phases. The tetragonal phase is exits below 620 °C, and changes to the orthorhombic form over 620 °C, whereas the AgIn₅S₈ has only the cubic spinel-type structure. AgInS₂ or AgIn₅S₈ films on various substrates have been prepared by pulse laser vaporization, chemical spray pyrolysis, chemical bath deposition, vacuum evaporation, sulphurization of Ag-In alloy films, aerosol-assisted chemical vapour deposition from a single precursor solution, and coevaporation. Among these, evaporation and sulphurization methods have better control over the compositions of the films compared to solution-based techniques, such as spray pyrolysis and chemical bath deposition. However, the convenient experimental apparatus and the ability to grow larger films at a lower temperature make the solution growth processes attractive for industrial applications. Nevertheless, there are few reports in the literature which selectively prepare a single phase of AgInS₂ as well as a single phase of AgIn₅S₈ film from an aqueous solution by adjusting preparative parameters. In this report, chemical bath deposition was employed to deposit silver indium sulfide thin films on self-assembled monolayer (SAM)-modified glass substrates.

4.3.1 Deposition of silver indium sulfide from [AgS₂CN(Me)(CH₂)₃N(Me)₂] and [In(S₂CN(Me)(CH₂)₃N(Me)₂)₃]

A 1:1 stoichiometric mixture of single source precursors [AgS₂CN(Me)(CH₂)₃N(Me)₂] and [In(S₂CN(Me)(CH₂)₃N(Me)₂)₃] was used in a THF solution to deposit AgInS₂ thin films onto glass substrates by AACVD method.

4.3.1.1 p-XRD of silver indium sulfide thin films

The p-XRD patterns for the films deposited at 300, 400 and 500 °C are shown in Figure 4-25. The deposition at all temperature give the same material. The peaks are indexed to cubic AgIn₅S₈ (ICDD card No. 00-026-1477). The peaks are considerably broader for the films deposited at 300 and 400 °C but the sharpness and the intensity of the peaks increased for the films deposited at 500 °C.
Figure 4-25: p-XRD diagram of silver indium sulfide films deposited by AACVD from \([\text{AgS}_2\text{CN(Me)(CH}_2_3\text{N(Me)}_2]\) and \([\text{In(S}_2\text{CN(Me)(CH}_2_3\text{N(Me)}_2)]\) at 300 °C, 400 °C and 500 °C. Peaks indexed to cubic AgInS\(_8\) (ICDD card No. 00-026-1477).

4.3.1.2 SEM of silver indium sulfide thin films

SEM Images of the films deposited at 300, 400 and 500 °C are shown Figure 4-26, Figure 4-28, and Figure 4-30. Elongated shaped crystals were shown by SEM images for the film deposited at 300 °C (Figure 4-26) whereas the shape of crystallites changed to more spherical at the higher deposition temperatures of 400 and 500 °C (Figure 4-28 and Figure 4-30).

Energy Dispersive X-Ray spectroscopy analysis, of the films deposited at 300 °C show the composition ratio of (Ag:In:S) as (~ 10:49:41) (~ 1:5:4) (Figure 4-26) those deposited at 400 °C as (10:50:40) (1:5:4) (Figure 4-28) and those deposited at 500 °C as (12:42:46) (1:4:4) (Figure 4-30). The elemental mapping of silver indium sulfide thin films for films deposited at 300, 400 and 500 °C are shown in Figure 4-27, Figure 4-29 and Figure 4-31 respectively.
Figure 4-26: SEM images (a, b with different magnification) and (c) EDAX spectrum of silver indium sulfide thin films deposited from [Ag(S$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$)] and [In(S$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$)$_3$] at 300 °C by AACVD.

The images show the distribution of Ag, In, and S in each Figure.

Figure 4-27: The elemental mapping of silver indium sulfide thin film, (a) shows distribution of Ag, In, and S, (b) shows Ag, (c) shows In and (d) shows S for the films deposited at 300°C.
Figure 4-28: SEM images (a, b with different magnification) and (c) EDAX spectrum of silver indium sulfide thin films deposited from [Ag(S$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$)] and [In(S$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$)$_3$] at 400 °C by AACVD.

Figure 4-29: The elemental mapping of silver indium sulfide thin film (a) shows distribution of Ag, In, and S, (b) shows Ag, (c) shows In and (d) shows S for the films deposited at 400°C.
Figure 4-30: SEM images (a, b with different magnification) and (c) EDAX spectrum of silver indium sulfide thin films deposited from [Ag(S₂CN(Me)(CH₂)₃N(Me)₂)] and [In(S₂CN(Me)(CH₂)₃N(Me)₂)₃] at 500 °C by AACVD.

Figure 4-31: The elemental mapping of silver indium sulfide thin film, (a) shows distribution of Ag, In, and S, (b) shows Ag, (c) shows In and (d) shows S for the films deposited at 500°C.
4.3.1.3 **AFM of silver indium sulfide thin films**

The AFM images of the films deposited at 300, 400 and 500 °C from [Ag(S₂CN(Me)(CH₂)₃N(Me)₂)] and [In(S₂CN(Me)(CH₂)₃N(Me)₂)₃] are shown in Figure 4-32, Figure 4-33 and Figure 4-34 respectively.

The height of roughness of the surface for the films deposited at 300, 400 and 500 °C was observed as 425, 324, and 24 nm respectively. It is interesting to note that the films with the largest crystallites showed the most even surface as opposed to those observed for copperindium sulfide films. The films deposited at the lowest temperature showed the most uneven surface in this case (Figure 4-32(b)).

![AFM images](image.png)

**Figure 4-32:** (a) AFM images (2D and 3D) of films deposited at 300 °C from \textit{tris}(trimethylpropylenediaminodithiocarbamato)indium(III) and trimethylpropylenediaminodithiocarbamatosilver(I) and (b) Root Mean Square of height of crystallisation.
Figure 4-33:  (a) AFM images (2D and 3D) of films deposited at 400 °C from \textit{tris}(trimethylpropylenediaminodithiocarbamato)indium(III) and trimethylpropylene-diaminodithiocarbamatosilver(I), (b) Root Mean Square of height of crystallisation.
Figure 4-34: (a) AFM images (2D and 3D) of films deposited at 500 °C from $tris$(trimethylpropylenediaminodithiocarbamato)indium(III) and trimethylpropylendiaminodithiocarbamatosilver(I), (b) Root Mean Square of height of crystallisation.

### 4.4 Cadmium zinc sulfide

Zinc sulfide has two main forms the cubic (sphalarite) and hexagonal (wurtzite); in addition to these other polytypes are known. These forms differ in the packing arrangement of the layers. Optical studies on the polytypes indicate that the absorption edge and the birefringence can be correlated with the percentage of
hexagonally stacked planes in the unit cell. The optical band gap of cubic ZnS 3.5eV shifts to higher values with increasing pressure. ZnS is used as a phosphor with Cu, Mn, Ag added as activator or co-activator.

CdS normally exists in hexagonal (greenockite) or cubic (hawleyite) forms at high pressure CdS transforms to an NaCl (halite) type structure. Structural changes in CdS occur on electron irradiation. CdS has interesting semiconducting and photoconducting properties. The mobility of charge carriers is strongly dependent upon temperature due to phonon scattering, and in addition to polar acoustic modes at low temperature. Measurements of photo Hall effect indicate that Hall mobility increases with increasing carrier concentration by photon excitation. In the wurtzite structure, CdS has band gap of 2.58 eV which increase with increasing pressure. The band structure of CdS is calculated to be similar to that of ZnS. The photo sensitivity of CdS can be altered by doping with impurities such as copper or iodide.

ZnS or CdS thin films have been used for a wide variety of technological applications including in: photovoltaic cells, electro-optic modulators, sensors, electroluminescent and photo luminescent devices and anti-reflection coatings. In particular they have been widely employed in display technology as host lattices for doped phosphor materials, whose emission wave length can be tailored as a function of the dopant metal. The size and electronic structure of the cations added are sufficiently similar to Cd and/or Zn for the formation of solid solutions. Thus, these are systems in which systematic variation of photoelectronic properties are possible simply by adjusting composition.

In the wurtzitic structure ZnS and CdS have unit cell volumes in the ratio 0.77. Because of such similarities these materials have been widely employed in p-n junction with a relatively small lattice mismatch in device based on quaternary materials like CuInₓGa₁₋ₓSe₂ or CuIn(SₓSe₁₋ₓ)₂. Thin films of ZnₓCd₁₋ₓS have properties between those of ZnS and CdS. ZnS has a larger bandgap than CdS so all the ZnₓCd₁₋ₓS ternaries have larger energy bandgaps than CdS which can make the materials attractive as windows in hetero junction photovoltaic derived such as
CdS/CdTe solar cells.\textsuperscript{110-115} Recently, Wang \textit{et al.} detailed the use of ZnCdS in memory devices.\textsuperscript{116}

The route used to prepare or deposit a material can profoundly affect phase composition, as well as thermal stability and morphology which can in turn influence the functional behaviour of the material. Many techniques have been used including: sputtering,\textsuperscript{117,118} pulsed laser ablation,\textsuperscript{119,120} spray pyrolysis,\textsuperscript{121,122} chemical bath deposition,\textsuperscript{123,124} electrostatic assisted aerosol jet deposition,\textsuperscript{124,125} sol-gel,\textsuperscript{126,127} ion-beam deposition\textsuperscript{128} and MOCVD.\textsuperscript{129-137} MOCVD is well known to give high quality thin films. Various single source precursors have been investigated including: metal complexes of dialkyldithiocarbamates,\textsuperscript{131-134} alkyl xanthates\textsuperscript{135} and dimorpholino dithioacetylacetonates.\textsuperscript{120} Recently it has been demonstrated that thio- and dithio-biuret metal complexes can be used as single source precursors for the preparation of various metal sulfide thin films\textsuperscript{136-140} and nanoparticles.\textsuperscript{141} Moreover, in the lab, Zn and Cd complexes of 1,1,5,5–tetraalkyl-2-4-dithiobiurets (R = methyl or ethyl) and 1,1,5,5–tetraalkyl-2-thiobiurets (R = isopropyl) were synthesized and used as a single molecular precursors for deposition ZnS, CdS and Zn\textsubscript{x}Cd\textsubscript{1-x}S thin films by AACVD.\textsuperscript{142}

\subsection*{4.4.1 AACVD deposition of CdZnS thin films from \([Cd(S_2CN(Me)(CH_2)_3N(Me)_2)_2]\) and \([Zn(S_2CN(Me)(CH_2)_3N(Me)_2)_2]\)

A mixture of single source precursors \([Cd(S_2CN(Me)(CH_2)_3N(Me)_2)_2]\) and \([Zn(S_2CN(Me)(CH_2)_3N(Me)_2)_2]\) was used to deposit cadmium zinc sulfide thin films onto glass substrates by AACVD method. The deposition details are given in the experimental section (chapter 5).

\subsection*{4.4.1.1 p- XRD of CdZnS thin films}

The p-XRD patterns for the films deposited at 300, 400 and 500 °C are shown in Figure 4-35. The deposition of the films at lower temperature of 300 °C gave broad p-XRD peaks but those deposited at 400 and 500 °C showed sharper and more intense peak also showing more preferred orientation. Peaks at all deposition temperature were observed in between the values for hexagonal CdS (ICDD card No. 01-080-0006) and wurtzite ZnS (ICDD card No. 00-001-0677).
Figure 4-35: p-XRD pattern of cadmium zinc sulfide films deposited by AACVD from \([\text{Cd(S}_2\text{CN(Me)(CH}_2\text{}_3\text{N(Me)}_2\text{)}_2]\] and \([\text{Zn(S}_2\text{CN(Me)(CH}_2\text{}_3\text{N(Me)}_2\text{)}_2]\] at 300 °C, 400 °C and 500 °C. What was shown, was that in between a mixture of hexagonal CdS (ICDD card No. 01-080-0006) and wurtzite, an alpha hexagonal ZnS, (ICDD card No. 00-001-0677).

4.4.1.2 SEM, EDAX and elemental mapping images of CdZnS thin films

SEM images of the films deposited at 300 °C are shown in Figure 4-36. The image shows the deposition of granular crystals which fuse together to form the clusters. The size of these clusters appeared to be around 100 nm. Energy Dispersive X-Ray spectroscopy analysis, of the films deposited at 300 °C show that the composition ratio of (Cd:Zn:S0 is: (~ 46:30:25) (~ 2:1:1) at 300 °C (Figure 4-36 (c)).

The SEM images of the films deposited at 400 °C showed similar shaped crystals with a similar morphology of the films. Energy Dispersive X-Ray spectroscopy analysis, of the films showed that the composition ratio of (Cd:Zn:S) is: (39:33:28) (~ 1:1:1) (Figure 4-38). The elemental mapping of thin films deposited at 400 °C is shown in (Figure 4-39) which shows the almost equal colour for cadmium, zinc and sulfur.
Figure 4-36: SEM images (a, b with different magnification) and (c) EDAX spectrum of cadmium zinc sulfide thin films deposited from \([\text{Cd}(\text{S}_2\text{CN(Me)})(\text{CH}_2)_3\text{N(Me)}_2)]\) and \([\text{Zn}(\text{S}_2\text{CN(Me)})(\text{CH}_2)_3\text{N(Me)}_2)]\) at 300 °C by AACVD.

Figure 4-37: The elemental mapping of thin film, (a) shows distribution of Cd, Zn, and S, (b) shows Cd, (c) shows Zn and (d) shows S for films deposited at 300 °C.
Figure 4-38: SEM images (a, b with different magnification) and (c) EDAX spectrum of cadmium zinc sulfide thin films deposited from [Cd(S$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$)$_2$] and [Zn(S$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$)$_2$] at 400 °C by AACVD.

Figure 4-39: The elemental mapping of thin film, (a) shows distribution of Cd, Zn, and S, (b) shows Cd, (c) shows Zn and (d) shows S for the films deposited at 400°C.
Figure 4-40: SEM images (a, b with different magnification) and (c) EDAX spectrum of cadmium zinc sulfide thin films deposited from [Cd(S₂CN(Me)(CH₂)₃N(Me)₂)] and [Zn(S₂CN(Me)(CH₂)₃N(Me)₂)] at 500 °C by AACVD.

The SEM images of the films deposited at 500 °C are much smoother than those deposited at 300 or 400 °C. The EDAX spectrum showed the (Cd:Zn:S) as (15:41:44) (~ 1:3:3) (Figure 4-40). The elemental mapping of the thin films is shown in Figure 4-41.
Figure 4-41: The elemental mapping of thin film, (a) shows distribution of Cd, Zn, and S, (b) shows Cd, (c) shows Zn and (d) shows S for the films deposited at 500°C.

4.4.1.3 AFM of the CdZnS thin films

The AFM images of the films deposited by AACVD at 300, 400 and 500 °C from [Cd(S₂CN(Me)(CH₂)₃N(Me)₂)₂] and [Zn(S₂CN(Me)(CH₂)₃N(Me)₂)₂] are shown in Figure 4-42, Figure 4-43 and Figure 4-44 respectively.

Figure 4-42: (a) AFM images (2D and 3D) of cadmium zinc sulfide films deposited at 300 °C from bis(trimethylpropylenediaminodithiocarbamato)cadmium(II) and bis(trimethylpropylenediaminodithiocarbamato)zinc(II) and (b) Root Mean Square of height of crystallisation.
The height of roughness of the surface for the films deposited at 300, 400 and 500 °C was observed as 160, 17.7, and 78 nm respectively. These films are much smoother than those deposited for silver indium sulfide or copper indium sulfide at similar temperatures.

![Image](image_url)

Figure 4-43: (a) AFM images (2D and 3D) of cadmium zinc sulfide films deposited at 400 °C from bis(trimethylpropylenediaminodithiocarbamato)cadmium(II) and bis(trimethylpropylenediaminodithiocarbamato)zinc(II) and (b) Root Mean Square of height of crystallisation.
Figure 4-44: (a) AFM images (2D and 3D) of cadmium zinc sulfide films deposited at 500 °C from \textit{bis}(trimethylpropylenediaminodithiocarbamato)cadmium(II) and \textit{bis}(trimethylpropylenediaminodithiocarbamato)zinc(II) and (b) Root Mean Square of height of crystallisation.
4.5 Conclusion

The X-ray structures of both indium compounds \([\text{In(S}_2\text{CN(Me)(CH}_2)_n\text{N(Me)}_2\text{)}_3]\) (\(n = 2, 3\)) were based on a monomer in which indium atom is coordinated to six sulphur atoms of three chelating thiocarbamato ligands. The six sulphur atoms from three chelating dithiocarbamato ligands are arranged in a distorted octahedral environment around the central metal atom. Both complexes decompose in a clean single step to give about 20% residue which corresponds to indium sulfide. \([\text{In(S}_2\text{CN(Me)(CH}_2)_2\text{N(Me)}_2\text{)}_3]\) decomposed at almost 100 °C lower (190 °C) than the \([\text{In(S}_2\text{CN(Me)(CH}_2)_3\text{N(Me)}_2\text{)}_3]\) (290 °C). Indium sulfide deposited at 300 or 400 °C gave a broad peak indicating the nanocrystal size of the deposited material (tetragonal \(\text{In}_2\text{S}_3\)). The morphology of the films consists of spherical particles with the size range of 300-400 nm densely packed on the surface of the substrate. p-XRD pattern of the films deposited by AACVD from the mixture of \(\text{Cu(S}_2\text{CN(Me)(CH}_2)_3\text{N(Me)}_2\text{)}_2\) and \([\text{In(S}_2\text{CN(Me)(CH}_2)_3\text{N(Me)}_2\text{)}_3]\) at 300 °C, 400 °C, and 500 °C showed the deposition of monoclinic \(\text{Cu}_{1.701}\text{In}_{0.05}\text{S}\). This was against the expected material (\(\text{CuInS}_2\)). Combination of silver and indium precursors gave cubic \(\text{AgIn}_5\text{S}_8\). The peaks are considerably broader for the films deposited at 300 and 400 °C but the sharpness and the intensity of the peaks increased for the films deposited at 500 °C. Those deposited from the combination of zinc and cadmium precursors showed the XRD peaks in between the values for hexagonal \(\text{CdS}\) (ICDD card No. 01-080-0006) and wurtzite \(\text{ZnS}\) (ICDD card No. 00-001-0677) at all deposition temperatures.
4.6 References:


142. A. Abd lhady, M. A. Malik, P. O’Brien unpublished work.
Chapter 5: Experimental
5.1 Chemicals
Zinc nitrate, \(N,N,N\)-trimethyethylenediamine, \(N,N,N\)-trimethypropylene-diamine, sodium hydroxide, carbon disulfide, sodium hydroxide, methanol, carbon disulfide, nickel chloride, copper nitrate, cobalt nitrate, indium chloride, cadmium acetate, silver nitrate and d-chloroform were used as purchased from Sigma Aldrich. Acetonitrile, chloroform, methanol, toluene and tetrahydrofuran were purchased from Fisher Chemicals.

5.2 Handling of air-sensitive compounds
The syntheses were carried out in an inert atmosphere using a double manifold Schlenk-line, attached to an Edwards E2M8 vacuum pump, and a dry nitrogen cylinder. All flasks were evacuated, and then purged with nitrogen at least three times prior to use, with external heat applied where deemed necessary. Solid air-sensitive compounds were handled inside a glove box under an atmosphere of dry nitrogen. Liquid air-sensitive chemicals were transferred to Schlenk type flask either by cannula or using syringes. Dry solvents, were either distilled over standard drying agents (Na/benzophenone, CaH\(_2\) etc.) or purchased and stored in flasks over molecular sieves.

5.3 Deposition of films by AACVD
In a typical experiment 0.25 mmol of the complex was dissolved in 20 mL tetrahydrofuran in a two-necked 100 mL round-bottom flask with a gas inlet that allowed the carrier gas (argon) to pass into the solution to aid the transport of the aerosol. This flask was connected to the reactor tube by a piece of reinforced tubing. The argon flow rate was controlled by a Platon flow gauge. Seven glass substrates (approx. 1 x 3 cm) were placed inside the reactor tube, which is placed in a CARBOLITE furnace. The precursor solution in a round-bottom flask was kept in a water bath above the piezoelectric modulator of a PIFCO ultrasonic humidifier (Model No. 1077). The aerosol droplets of the precursor thus generated were transferred into the hot wall zone of the reactor by carrier gas. Both the solvent and the precursor were evaporated and the precursor vapour reached the heated substrate surface where thermally induced reactions and film deposition took place.
5.4 Aerosol-Assisted Chemical Vapour Deposition (AACVD) methods

AA-CVD of the precursors were carried out in a custom-made AA-CVD kit. (Figure 5-1). The substrates were placed along the reaction chamber, which was inserted into a furnace. Solution of precursor in toluene or THF was put in a round-bottomed flask. The aerosol droplets was generated from the precursor solution by mean an ultrasonic humidifier. Flow of carrier gas (Ar) transferred the aerosol droplets to the deposition chamber where film deposition take place.

![AACVD Kit](image)

Figure 5-1: Schematic diagram of AA-MOCVD kit.

5.5 Cleaning of glass substrates

The substrate used was glass microscope slides, cut to size (1 x 3 cm²) by hand. The glass substrates used in this work were cleaned using the following procedure

(a) Glass substrates were degreased in trichloroethylene and placed in acetone to remove organic residues.

(b) Then the substrates were rinsed in deionised water.

(c) The rinsed substrates were placed in 50% nitric acid for overnight and then ultrasonicated for further 10 minutes in deionised water.
(d) Finally, they were rinsed again in deionised water and oven-dried.

5.6 Characterization methods
NMR spectra were recorded using a Bruker AC300 FT-NMR spectrometer, using CDCl$_3$ as solvent. $^1$H NMR spectra were referenced to the solvent signal and the chemical shifts are reported relative to Me$_4$Si.

Infrared spectra were recorded on a Perkin Elmer Spectrum BX FT-IR spectrometer. Mass spectra were recorded on a Micromass platform II instrument by atmospheric pressure chemical ionization (APCI) method.

5.7 Thermogravimetric analysis
Thermogravimetric analysis measurements were carried out by a Seiko SSC/S200 model under a heating rate of 10 °C min$^{-1}$ under nitrogen. Indium metal is used as a reference to calibrate the instrument. TGA was performed by school of chemistry microanalysis team.

5.8 Elemental analysis
CHNS analysis is carried out on a Carlo Erba EA 1108 elemental analyser which is calibrated with standard reference material (acetanilide). The sample is placed in a tin container which is dropped into a furnace at 1000 °C and then oxygen ejected from furnace. The sample burns and decomposes forming carbon dioxide (C), water vapour (H), nitrogen (N) and sulphur dioxide. These gases are analysed in a gas chromatography (GC) column to determine the amount of each element present in the sample. Metals (Cu, Ag, Co, Ni, Zn and Cd, In ) analysis were carried out by adding acid to the weighed quantity of the sample placed in a tube. This is heated to the temperature at which the sample is digested and decomposed by the acid. The residue is transferred to volumetric flask containing water. This solution is analysed by Fisons Horizon ICP-OES which measures the concentration of each element in the solution. Elemental analysis were performed by school of chemistry microanalysis team.

5.9 X-ray diffraction (XRD)
p-XRD is used for the identification, purity and phase of a crystalline material. It is a rapid, non-destructive method and it is based on constructive interference of X-rays.
and a sample. The X-rays generated by a cathode ray tube are filtered and directed to the sample. Diffracted X-rays are produced when Bragg’s Law is satisfied \((n\lambda=2d \sin \theta)\). Where \(\lambda\) is the wavelength of x-ray, \(n\) is the order, \(d\) is the spacing between two crystal planes and \(\theta\) the diffraction angle, Figure 5-2. The identification is achieved by processing the diffracted rays. These diffracted rays \((2\theta)\) are converted to \(d\)- spacings which are then matched with standard reference patterns stored in the ICDD (International Centre for Diffraction Data) database.

Figure 5-2: Schematic of X-ray diffractometer.

An X-ray diffractometer is comprised principally of an X-ray tube, a sample holder and an X-ray detector/monitor. In the X-ray tube, lies a cathode ray tube which generates electrons; these are accelerated towards a metal anode target by applying a potential difference. Incident electrons with sufficient energy remove inner shell electrons of the metal atoms in the anode and therefore X-rays are emitted which are then directed towards the sample. Typical anode materials include Cu (most common), Co, Mo, Fe and Cr. Another application of XRD is in the determination of crystallite size. This can be done by evaluating the broadness of the peak using the Scherrer equation, Equation 5-1:

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

Equation 5-1
Where $D$ is the particle diameter, $K$ is Scherrer constant, $\lambda$ is the wavelength, $\theta$ is the angle of diffraction and $\beta$ is the Full width at half maximum (FWHM) of a reflection.

X-ray diffraction studies were performed on a Bruker AXS D8 diffractometer using Cu-K$\alpha$ radiation. The samples were mounted flat and scanned between 20 to 80° in a step size of 0.05 with a count rate of 9 sec. The diffraction patterns were then compared to the documented patterns in the ICDD index.

5.10 Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

EDX is an analytical tool which is used to determine the elemental composition of a sample in a TEM or Scanning electron microscope (SEM). It works on the principle that each element has a unique electronic structure which gives rise to a unique pattern of peaks when it interacts with electromagnetic radiations.

EDX, Figure 5-3, is done by focusing a high energy electron beam on a sample; this beam removes an electron from the inner shell thereby creating a hole. This hole is then filled by an electron from a higher energy shell and the difference in energy may be released in the form of X-ray fluorescence which is then measured by the spectrometer. EDX is used qualitatively by assigning the energies of X-rays emitted to corresponding elements present.
Films were carbon coated using Edward’s E306A coating system before carrying out SEM and EDX analyses. SEM analysis was performed using a Philips XL 30FEG and EDX was carried out using a DX4 instrument.

5.11 Atomic Force Microscopy
The atomic force microscopy (AFM) analysis of the thin films was carried using a Veeco CP2 instrument.

5.12 Single crystal X-ray structure determination
Single-crystal X-ray diffraction data for the compounds were collected using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Bruker APEX diffractometer. The structure was solved by direct methods and refined by full-matrix least squares on F². All non-H atoms were refined anisotropically. H atoms were included in calculated positions, assigned isotropic thermal parameters and allowed to ride on their parent carbon atoms. All calculations were carried out using the SHELXTL package. Single crystal X-ray diffraction data collection and structure determination were performed by Dr. James Raftery or Dr. Madeleine Helliwell.
5.13 Synthesis

5.13.1 Synthesis of N,N-Dimethylimidazolidine-2-thione (DMIT) (1).

In a typical experiment a mixture of sodium hydroxide (0.6 g, 14.7 mmol) and N,N,N-trimethylethylenediamine (1.5 g, 14.7 mmol) in methanol (50 ml) was stirred at room temperature until all NaOH was dissolved. The mixture was cooled to 0 °C in an ice bath and a solution of carbon disulfide (1.2 g, 14.7 mmol) in methanol (25 ml) separately cooled in a beaker was added dropwise into it while stirring vigorously. After addition of all carbon disulfide, the reaction mixture was allowed to warm at room temperature while stirring. Equation 2-1.

Elemental analysis (Found: C, 33.30; H, 6.24; N, 12.10; S, 25.81. Calc. C, 33.96; H, 6.13; N, 13.21; S, 30.19%).

5.13.2 Synthesis of bis(trimethylethylenediaminodithiocarbamato)zinc(II): [Zn(S₂CN(Me)(CH₂)₂N(Me)₂)₂] (2).

In a typical experiment a mixture of sodium hydroxide (0.6 g, 14.7 mmol) and N,N,N-trimethylethylenediamine (1.5 g, 14.7 mmol) in methanol (50 ml) was stirred at room temperature until all NaOH was dissolved. The mixture was cooled to 0 °C in an ice bath and a solution of carbon disulfide (1.2 g, 14.7 mmol) in methanol (25 ml) separately cooled in a beaker was added dropwise into it while stirring vigorously. After addition of all carbon disulfide, the reaction mixture was allowed to warm at room temperature while stirring. After about 20 minutes a solution of zinc nitrate (1.4 g, 7.3 mmol) in water (50 ml) was added dropwise into it while stirring. A white precipitate formed, which was separated by filtration. The precipitate was washed with excess of water to remove any unreacted impurities and first dried on a filter paper in air and then under vacuum. The product was later recrystallised from hot toluene to give white cubic crystals. Equation 2-2.

Yield (%): 45, m.p:140 °C, a white solid product was obtained.

Elemental analysis (Found: C, 33.43; H, 6.89; N, 12.67; S, 31.34. Zn, 15.67. Calc. C, 34.37; H, 6.21; N, 13.37; S, 30.55. Zn, 15.51. %); IR (cm⁻¹): 470(Zn-S), 991(C-S), 1495(C=N); ¹H NMR solution δ(ppm): 2.23 [12H,s,N(CH₃)] 2.62 [4H, t,
(CH$_3$)$_2$NCH$_3$, 3.41 [6H, s, NCH$_3$], 3.92 [4H, t, NCH$_2$CH$_2$]; $^{13}$C NMR (solid state) δ(ppm): 44.16 [N(CH$_3$)$_2$], 45.78 [(CH$_3$)$_2$NCH$_2$], 55.02 [NCH$_3$], 55.70 [NCH$_3$CH$_2$].

5.13.3 Synthesis of *bis*(trimethylpropylenediaminodithiocarbamato)zinc(II):

[Zn(S$_2$CN(Me)(CH$_2$)$_2$N(Me)$_2$)$_2$] (3)

By the same method as used for the preparation of (2) but used N,N,N-trimethylpropylenediamine. Equation 2-2.

% yield: 35, m.p: 143 °C, a white solid crystalline product was recrystallised from toluene.

Elemental analysis (Found: C, 36.99; H, 6.55; N, 12.35; S, 29.44. Zn, 14.67. Calc. C, 37.58; H, 6.71; N, 12.53; S, 28.64. Zn, 14.54. %); IR (cm$^{-1}$): 490 (Zn-S), 995 (C-S), 1490 (C=N); $^1$H NMR solution δ(ppm): 1.97 [4H, m, CH$_2$CH$_2$CH$_2$], 2.29 [12H, s, N(CH$_3$)$_2$], 2.43 [4H, t, CHNCH$_2$], 3.37 [6H, s, NCH$_3$], 3.86 [4H, t, NCH$_2$CH$_2$]; $^{13}$C NMR (solid state) δ(ppm): 25.02 [NCH$_3$], 42.90 [CH$_2$CH$_2$CH$_2$], 46.08 [N(CH$_3$)$_2$], 55.50 [CH$_2$CH$_2$N], 57.20 [NCH$_2$CH$_2$], 204.2 [CS$_2$].

5.13.4 Synthesis of *bis*(trimethyleneethylenediaminedithiocarbamato)cadmium(II):

[Cd(S$_2$CN(Me)(CH$_2$)$_2$N(Me)$_2$)$_2$] (4)

A mixture of sodium hydroxide (14.7 mmol) and N,N,N-trimethyleneethylenediamine (14.7 mmol) in methanol (50 ml) was stirred at room temperature until all NaOH was dissolved. The mixture was cooled to 0 °C in an ice bath and a solution of carbon disulfide (14.7 mmol) in methanol (25 ml) cooled in a separate beaker was added dropwise into it while stirring vigorously. After addition of all carbon disulfide, the reaction mixture was allowed to warm at room temperature while stirring. After about 20 minutes a solution of cadmium acetate (7.3 mmol) in water (50 ml) was added dropwise into it while stirring. A white precipitate formed, which was separated by filtration. The precipitate was washed with excess of water to remove any unreacted impurities and first dried on a filter paper in air and then under vacuum. The product was later recrystallised from hot toluene to give white crystals. Equation 2-2.

% yield: 36, m.p: 140 °C, a white solid product was obtained.
Elemental analysis (Found: C, 30.05; H, 5.62; N, 10.92; S, 29.80. Cd, 23.61. Calc. C, 30.87; H, 5.57; N, 12.00; S, 27.44. Cd, 24.10. %); IR (cm$^{-1}$): 435(Cd-S), 1011(C-S), 1442(C=N). $^1$H NMR solution δ(ppm): 2.05 [12H,s ,N(CH$_3$)$_2$], 2.75 [4H,t, (CH$_3$)$_2$NCH$_2$], 3.45 [6H,s, NCH$_3$], 4.1 [4H,t, NCH$_3$CH$_2$ ]. $^{13}$C NMR (solid state ) δ(ppm):, 36.28 [(CH$_3$)$_2$NCH$_2$], 47.51 [NCH$_3$], 56.49 [NCH$_3$CH$_2$], 179.95 [CS$_2$].

5.13.5 Synthesis of bis(trimethylpropylenediaminedithiocarbamato)cadmium(II): [Cd(S$_2$CN(Me)(CH$_2$)$_3$N(Me)$_2$)$_2$] (5)

Compound (5) was prepared by the same method as compound (4) but used $N,N,N$-trimethylpropylenediamine. Equation 2-2.

% yield: 26, m.p: 129°C, a white solid product was obtained.

Elemental analysis (Found: C, 33.67; H, 6.20; N, 10.44; S, 26.23. Cd, 23.46. Calc. C, 33.98; H, 6.07; N, 11.33; S, 25.89. Cd, 22.74. %); IR (cm$^{-1}$): 425(Cd-S), 961(C-S), 1425(C=N). $^1$H NMR solution δ(ppm): 2.05 [12H,s ,N(CH$_3$)$_2$], 2.15 [12H,s ,N(CH$_3$)$_2$], 2.55 [4H,m,CHNCH$_2$], 3.45 [6H,s, NCH$_3$], 3.95 [4H,t, NCH$_3$CH$_2$ ]. $^{13}$C NMR (solid state ) δ(ppm): 30.95[NCH$_3$], 46.03[N(CH$_3$)$_2$], 57.37[NCH$_3$CH$_2$], 205.68[CS$_2$].

5.13.6 Synthesis of bis(trimethylethylenediaminedithiocarbamato)nickel(II):

[Ni(S$_2$CN(Me)(CH$_2$)$_2$N(Me)$_2$)$_2$] (6)

A mixture of sodium hydroxide (14.7 mmol) and $N,N,N$-trimethylethylenediamine (14.7 mmol) in methanol (50 ml) was stirred at room temperature until all NaOH was dissolved. The mixture was cooled to 0 °C in an ice bath and a solution of carbon disulfide (14.7 mmol) in methanol (25 ml) cooled in a separate beaker was added dropwise into it while stirring vigorously. After addition of all carbon disulfide, the reaction mixture was allowed to warm at room temperature while stirring. After about 20 minutes a solution of NiCl$_2$ .6H$_2$O ( 7.3 mmol) in water (50 ml) was added dropwise into it while stirring. A green precipitate formed, which was separated by filtration. The precipitate was washed with excess of water to remove any unreacted impurities and first dried on a filter paper in air and then under vacuum. The product was later recrystallised from hot toluene. Equation 2-2.
% yield: 63, m.p: 152 °C, a green solid product was obtained.

Elemental analysis (Found: C, 32.85; H, 6.50; N, 12.16; S, 28.30. Ni, 10.93. Calc. C, 34.89; H, 6.29; N, 13.57; S, 31.02. Ni, 14.22. %); IR (cm\(^{-1}\)): 490(Ni-S), 989(C-S), 1523(C=N).

5.13.7 Synthesis of \textit{bis}(trimethylpropylenediaminedithiocarbamato)nickel(II):

\[ \text{[Ni(S}_2\text{CN(Me)(CH}_2\text{)_3N(Me)}_2\text{)] (7)} \]

Compound (7) was synthesized by the same method as described for (6) but used \textit{N,N,N}-trimethylpropylenediamine. Equation 2-2.

% yield: 27, m.p: 156 °C, a green solid product was obtained.

Elemental analysis (Found: C, 37.89; H, 7.17; N, 12.32; S, 29.78. Ni, 12.62. Calc. C, 38.12; H, 6.81; N, 12.71; S, 29.04. Ni, 13.32. %); IR (cm\(^{-1}\)): 501(Ni-S), 962(C-S), 1450(C=N).

5.13.8 Synthesis of \textit{bis}(trimethylpropylenediaminedithiocarbamato)copper(II):

\[ \text{[Cu(S}_2\text{CN(Me)(CH}_2\text{)_3N(Me)}_2\text{)] (8)} \]

Sodium hydroxide (12 mmol) and \textit{N,N,N}-trimethylpropylenediamine (12 mmol) in methanol (50 ml) was stirred at room temperature until all NaOH was dissolved. The mixture was cooled to 0 °C in an ice bath and a solution of carbon disulfide (12 mmol) in methanol (25 ml) cooled in a separate beaker was added dropwise into it while stirring vigorously. After addition of all carbon disulfide, the reaction mixture was allowed to warm at room temperature while stirring. After about 20 minutes a solution of Cu(NO\(_3\))\(_2\).2.5H\(_2\)O (6 mmol) in water (50 ml) was added dropwise into it while stirring. A brown precipitate formed, which was separated by filtration. The precipitate was washed with excess of water to remove any unreacted impurities and first dried on a filter paper in air and then under vacuum. Equation 2-2.

% yield: 32, a brown paste.

Elemental analysis (Found: C, 37.39; H, 7.47; N, 12.06; S, 28.84. Cu, 15.13. Calc. C, 37.71; H, 6.73; N, 12.57; S, 28.73. Cu, 14.25. %); IR (cm\(^{-1}\)): 509(Cu-S), 987(C-S), 1519(C=N).
5.13.9 Synthesis of tris(trimethylethyleneaminedithiocarbamato)cobalt(III):

\[ \text{[Co(S}_2\text{CN(Me)(CH}_2\text{)}_2\text{N(Me)}_2\text{)}_3]} \quad (9) \\

Sodium hydroxide (10.5 mmol) and \( N,N,N \)-trimethylethyleneamidine (10.7 mmol) in methanol (40 ml) was stirred at room temperature until all NaOH was dissolved. The mixture was cooled to 0 °C in an ice bath and a solution of carbon disulfide (10.5 mmol) in methanol (25 ml) cooled in a separate beaker was added dropwise into it while stirring vigorously. After addition of all carbon disulfide, the reaction mixture was allowed to warm at room temperature while stirring. After about 20 minutes a solution of Co(NO\(_3\))\(_2\).6H\(_2\)O (5 mmol) in water (30 ml) was added dropwise into it while stirring. A dark green precipitate formed, which was separated by filtration. The precipitate was washed with excess of water to remove any unreacted impurities and first dried on a filter paper in air and then under vacuum. Equation 2-2.

% yield: 28, a dark green paste.

Elemental analysis (Found: C, 38.64; H, 6.91; N, 13.72; S, 32.30. Co, 8.43. Calc. C, 36.61; H, 6.61; N, 14.24; S, 32.54. Co, 10.00. %); IR (cm\(^{-1}\)) \( \nu \): 488(Co-S), 991(C-S), 1508(C=N).

5.13.10 Synthesis of tris(trimethylpropylenediaminedithiocarbamato)cobalt(III):

\[ \text{[Co(S}_2\text{CN(Me)(CH}_2\text{)}_3\text{N(Me)}_2\text{)}_3]} \quad (10) \\

Compound (10) was synthesized by the same method as described for (9) but used \( N,N,N \)-trimethylpropylenediamine. Equation 2-2.

% yield: 30, a dark green paste.

Elemental analysis (Found: C, 39.84; H, 7.72; N, 13.14; S, 31.24. Co, 8.06. Calc. C, 39.87; H, 7.12; N, 13.29; S, 30.38. Co, 9.34. %); IR (cm\(^{-1}\)) \( \nu \): 489(Co-S), 975(C-S), 1504(C=N).

5.13.11 Synthesis of tris(trimethylethyleneaminedithiocarbamato)indium(III):

\[ \text{[In(S}_2\text{CN(Me)(CH}_2\text{)}_2\text{N(Me)}_2\text{)}_3]} \quad (11) \\

Sodium hydroxide (12.5 mmol) and \( N,N,N \)-trimethylethyleneamidine (12.5 mmol) in methanol (50 ml) was stirred at room temperature until all NaOH was dissolved. The
mixture was cooled to 0 °C in an ice bath and a solution of carbon disulfide (12.5 mmol) in methanol (25 ml) cooled in a separate beaker was added dropwise into it while stirring vigorously. After addition of all carbon disulfide, the reaction mixture was allowed to warm at room temperature while stirring. After about 20 minutes a solution of InCl₃ (4 mmol) in water (30 ml) was added dropwise into it while stirring. A light yellow precipitate formed, which was separated by filtration. The precipitate was washed with excess of water to remove any unreacted impurities and first dried on a filter paper in air and then under vacuum. The product was then recrystallised from toluene to give light yellow needles. Equation 2-2.

% yield: 38, m.p:126°C, a light yellow solid product was obtained.

Elemental analysis (Found: C, 34.36; H, 6.05; N, 13.11; S, 29.45. In, 17.06. Calc. C, 33.44; H, 6.04; N, 13.00; S, 29.72. In, 17.80. %); IR (cm⁻¹): 501(In-S), 993(C-S), 1505(C=N). ¹H NMR solution δ(ppm): 2.11[18H ,NCH₃], 2.63 [6H,m, (CH₃)₂NCH₂], 3.38 [9H, NCH₃], 3.87 [6H,m,N CH₂CH₃]. ¹³C NMR (solid state ) δ(ppm): 44.72 [N(CH₃)₂ ] , 45.66[(CH₃)₂NCH₂ ], 55.67 [NCH₃ ] ,56.77 [NCH₂CH₂ ], 207.04 [CS₂ ].

5.13.12 Synthesis of tris(trimethylpropylenediaminedithiocarbamato)indium(III): [In(S₂CN(Me)(CH₂)₂N(Me)₂)₃] (12)

Compound (12) was synthesized by the same method as described for (11) but used N,N,N-trimethylpropylenediamine instead of N,N,N-trimethylethylenediamine. Equation 2-2.

% yield: 32, m.p:133 °C, a yellow solid product was obtained.

Elemental analysis (Found: C, 37.52; H, 6.91; N, 12.38; S, 27.62. In, 15.81. Calc. C, 36.63; H, 6.54; N, 12.21; S, 27.91. In, 16.72. %). IR (cm⁻¹): 505(In-S), 974(C-S), 1458(C=N). ¹H NMR solution δ(ppm): 1.89 [6H, d, CH₂CH₂CH₂], 2.11 [18H,s,N(CH₃)₂], 2.16 [6H,s,CH₂CH₂N ], 3.35 [9H,NCH₃ ].¹³C NMR (solid state ) δ(ppm): 31.01[NCH₃ ], 44.23 [CH₂CH₂CH₂ ], 45.47 [N(CH₃)₂ ], 56.57 [NCH₂CH₂ ] , 207.04 [CS₂ ].
5.13.13 Synthesis of (trimethylpropylenediaminedithiocarbamato)silver(I): 

\[ \text{[AgS}_2\text{CN(Me)(CH}_2\text{)}_3\text{N(Me)}_2\text{]} \quad (13) \]

Sodium hydroxide (11.5 mmol) and \(N,N,N\)-trimethylethylenediamine (11.5 mmol) in methanol (50 ml) was stirred at room temperature until all NaOH was dissolved. The mixture was cooled to 0 °C in an ice bath and a solution of carbon disulfide (11.5 mmol) in methanol (25 ml) cooled in a separate beaker was added dropwise into it while stirring vigorously. After addition of all carbon disulfide, the reaction mixture was allowed to warm at room temperature while stirring. After about 20 minutes a solution of AgNO\(_3\) (11.5 mmol) in water (30 ml) was added dropwise into it while stirring. A brown precipitate formed, which was separated by filtration. The precipitate was washed with excess of water to remove any unreacted impurities and first dried on a filter paper in air and then under vacuum. Equation 2-2.

AgNO\(_3\) instead of Zn(NO\(_3\))\(_2\). % yield: 37, a brown paste.

Elemental analysis (Found: C, 28.51; H, 5.21; N, 9.02; S, 21.31. Ag, 35.95. Calc. C, 28.09; H, 5.02; N, 9.36; S, 21.40. Ag, 36.12. %); IR (cm\(^{-1}\))\(^3\): 606 (Ag-S), 953(C-S), 1477(C=N). \(^1\)H NMR solution δ(ppm): 1.95 [2H, m, CH\(_2\)CH\(_2\)CH\(_2\)], 2.2 [6H, N(CH\(_3\))\(_2\)], 2.33 [2H,t,CH\(_2\)NCH\(_2\) ], 3.55 [3H,s,NCH\(_3\) ], 4.05 [2H,t,NCH\(_2\)CH\(_2\) ]. \(^{13}\)C NMR (solid state) δ(ppm): 30.96[NCH\(_3\) ], 49.46 [N(CH\(_3\))\(_2\) ], 206.36[CS\(_2\)].
5.14 References:


Chapter 6: Conclusion

and Future work
6.1 Conclusion
In this work twelve new metal complexes based on trimethylethylene-/-propylenediaminodithiocarbamatometal complexes with the general formulae
\[ \text{[M(S}_2\text{C(Me)} \text{(CH}_2\text{)}_n\text{N(Me)}_2\text{)}_2] (M = Zn, Cd, Cu, Ni; n = 2 or 3), \]
\[ \text{[M(S}_2\text{C(Me)} \text{(CH}_2\text{)}_n\text{N(Me)}_2\text{)}_3] (M = Co, In; n = 2 or 3), \]
\[ \text{[Ag(S}_2\text{C(Me)} \text{(CH}_2\text{)}_3\text{N(Me)}_2\text{)}_2] \]
have been synthesised and seven X-ray single crystal structures were determined. Most of these compounds were crystalline solids and stable for long periods of time. TGA of these compounds showed clean one step decomposition around 200 to 300 °C. The quality of the metal sulfide thin films deposited by AACVD method using these compounds as precursors showed them to be potentially useful single source precursors. All complexes deposited the corresponding metal sulfide thin films onto glass substrates. The films were deposited at different temperatures to observe the effect of deposition temperature on the morphology of films. SEM and AFM images of the films deposited at different temperatures showed clear differences in the shape and size of crystallites. Also the phase of the deposited material was highly effected by the change of deposition temperature specially in case of cobalt and nickel sulfides. The p-XRD pattern of the copper sulfide films deposited at all temperatures show the deposition of polycrystalline films of a mixture of tetragonal Cu\textsubscript{2}S and rhombohedral Cu\textsubscript{9}S\textsubscript{5} whereas the XRD peaks for silver sulfide thin films deposited at all three temperature were indexed to the monoclinic Ag\textsubscript{2}S. The p-XRD pattern of the cobalt sulfide thin films deposited at 300 °C showed the peaks corresponding to a mixture of cubic Co\textsubscript{3}S\textsubscript{4} and hexagonal beta CoS\textsubscript{1.097}. The films deposited at 400 °C and 500 °C showed comparatively sharper bands corresponding to only hexagonal beta CoS\textsubscript{1.097} phase.

The deposition of nickel sulfide thin films corresponds to a mixture of orthorhombic Ni\textsubscript{3}S\textsubscript{6} and hexagonal NiS\textsubscript{1.03} with dominant phase being NiS\textsubscript{1.03} depending on the deposition temperature. Combination of silver and indium precursors gave cubic AgIn\textsubscript{5}S\textsubscript{8}. Those deposited from the combination of zinc and cadmium precursors showed the XRD peaks in between the values for hexagonal CdS and wurtzite ZnS at all temperatures as expected.
6.2 Future work
This is the first time that a systematic work on these diamino derivatives of dithiocarbamatometal complexes has been carried out. Although considerable results have been achieved in this work but still it covers only a small amount of work on these complexes. I suggest the following for the future work.

1. Deposition of ternary or quarternary materials using different combination of these metal complexes. The work carried out in this thesis on ternary materials, is based only on preliminary results. This should be expanded using different ratios of precursors as each precursor has different reactivity.

2. All these metal complexes can be used for the preparation of metal sulfide nanoparticles by colloidal thermolysis. This can be a nice PhD project.

3. Other metal complexes should be prepared using these diamines.

4. Also diamines with the longer chain lengths than three should be used to prepare metal complexes. Interesting molecular structures can be expected from these complexes.

5. Metal complexes prepared with longer alkyl chain diamines dithiocarmates can be useful for self-capped nanoparticles.