The use of metal complexes to deposit metal chalcogenide thin films and nanoparticles

A Thesis presented by
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To the Department of Chemistry, University of Zululand
In fulfilment of the requirement for the award of the degree of
Doctor of Philosophy
In Chemistry

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STATEMENT OF SOURCES

DECLARATION

I hereby declare that this thesis is my own work and has not been submitted in any form for another degree or diploma at any university or other institution of tertiary education. Information derived from the published or unpublished work of others has been acknowledged in the text and a list of references is given.

[Signature]  

07/08/2006  

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ABSTRACT

This thesis consists of four chapters. The first chapter describes the properties, methods of deposition and applications of semiconductors. The second chapter focuses on the deposition of metal chalcogenides thin films from single molecular precursors of the type \([M\{N(EPR_2)\}_2]\), were \(M = \text{Pt, Pd, Ni; } E = \text{S or Se and } R = \text{^{1}Pr or Ph.}\) Ligands of the type \(R_2P(E)NP(E)R_2\), where \(R = \text{^{1}Pr or Ph were prepared to synthesize these precursors. Single X-ray structures of } [Pt\{N(^{1}Pr_2PSe)_2\}] \text{ and } [Pd\{N(SPh_2)_2\}] \text{ are reported and discussed. The X-ray structure of the platinum complex shows a square-planar conformation whereas the six membered PtSe}_2\text{P}_2N \text{ ring adopts a distorted “boat” conformation.}\)

The third chapter describes the deposition of metal sulphide thin films from \([M(S_2COR)_2], \text{ where } M = \text{Pt, Pd, Ni, Cd, Co, Cu and } R = \text{Et or } ^{1}\text{Pr. Single X-ray structures of } [M(S_2COR)_2], M = \text{Pt, Pd, and Ni , } R = \text{Et } \text{ are reported and discussed. The NiS thin films are polycrystalline and their } \theta \text{ values are in good agreement with the literature values. The phases do not seem to be affected by temperature whereas the morphology of the films changes with temperature. The morphology of the films has been found to be greatly influenced by varying the temperature. All the ligands and precursors were characterised by elemental analysis and by using spectroscopic techniques such as infrared (IR), mass spectrometry (MS), proton and carbon nuclear magnetic resonance (\(^1\text{H and } ^{13}\text{C NMR). Thin films of PtSe}_2, \text{ PdSe}_2, \text{ Pd}_4\text{Se}, \text{ Pd}_{17}\text{Se}_{15}, \text{ PdS, and PdS}_2 \text{ were deposited by aerosol assisted chemical vapour deposition (AACVD) and low pressure metal-organic vapour deposition (LP-MOCVD) using metal complexes of}}\).
iminobis(dialkylphosphinato)dichalcogenide ligands. Thin films of NiS, CdS, Pt, PdS, Pd_{16}S_{7}, and Co_{2}S_{8} were deposited by AACVD using the respective metal xanthate complexes. The films were characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX).

The fourth chapter focuses on the preparation of nanoparticles and nanorods from cadmium complexes. The synthesis of CdS nanoparticles and nanorods are described in detail. The synthetic route used for the synthesis of the CdS nanoparticles is the thermolysis of metal complexes, [Cd(S_{2}CNMe_{2})_{2}] and [Cd{SC(=S)OCH(CH_{3})_{2}}], in tri-octylphosphine oxide (TOPO) and hexadecylamine (HDA). The optical properties of the nanoparticles were studied by using ultraviolet (UV)-visible and photoluminescence (PL) spectroscopy. There were blue shifts in the band gaps for all CdS samples; however, photoluminescence was very poor. The hexagonal phase of CdS was observed for all CdS samples using XRD measurements. The transmission electron microscopy (TEM) images show that the TOPO capped CdS nanoparticles have a spherical shape whereas the HDA capped particles are rod shaped. Nanoparticles of CdS were characterised by UV-vis, PL, XRD and TEM.
CONTENTS

Title Page i
Declaration ii
Abstract iii
Contents v
List of tables xiii
List of figures xvi
List of abbreviations and Symbols xxii
Ligands and precursors prepared in this project xxiii
Techniques and methods xxiv
Symbols and constants xxv
Acknowledgements xxvii
Dedication xxix

CHAPTER 1: General introduction to semiconductor thin films

1.1 Background 2
1.2 Band theory 2
1.3 Theory of semiconductors 6
1.4 Deposition of semiconductor thin films 9
1.4.1 Thin film deposition techniques 9
1.4.2 Physical vapour deposition or vacuum deposition techniques 10
1.4.2.1 Physical vapour deposition by evaporation 11
1.4.2.2 Physical vapour deposition by sputtering
1.4.3 Chemical vapour deposition
1.4.3.1 Metal-Organic chemical vapour deposition
1.4.3.2 Aerosol-assisted chemical vapour deposition
1.4.4 Atomic layer deposition
1.4.5 Molecular beam epitaxy
1.5 Precursors for semiconductor thin films
1.6 Applications of semiconductor thin films
1.6.1 Microelectronics
1.6.2 Optoelectronics
1.6.3 Other applications

CHAPTER 2: Deposition of Platinum and Palladium chalcogenide thin films

2.1 General introduction
2.2 Experimental
2.2.1 Reagents
2.2.2 Synthesis of ligands
2.2.2.1 Synthesis of NH(SePPr₂)₂
2.2.2.2 Synthesis of NH(SPPr₂)₂
2.2.2.3 Synthesis of NH(SePPh₂)₂
2.2.2.4 Synthesis of NH(SPPh₂)₂
2.2.3 Synthesis of precursors
2.2.3.1 Synthesis of [Pt{N(SePPr₂)₂}]
2.2.3.2 Synthesis of \([\text{Pt}\{\text{N}(\text{SPPr}_2)\}_2]\) 36
2.2.3.3 Synthesis of \([\text{Pd}\{\text{N}(\text{SePPPr}_2)\}_2]\) 36
2.2.3.4 Synthesis of \([\text{Pd}\{\text{N}(\text{SPPr}_2)\}_2]\) 37
2.2.3.5 Synthesis of \([\text{Pd}\{\text{N}(\text{SePPPr}_2)\}_2]\) 37
2.2.3.6 Synthesis of \([\text{Pt}\{\text{N}(\text{SSPPr}_2)\}_2]\) 38
2.2.3.7 Synthesis of \([\text{Pd}\{\text{N}(\text{SSPPr}_2)\}_2]\) 38
2.2.3.8 Synthesis of \([\text{Pt}\{\text{N}(\text{SPPr}_2)\}_2]\) 39
2.2.3.9 Synthesis of \([\text{Ni}\{\text{N}(\text{SSPPr}_2)\}_2]\) 39
2.2.3.10 Synthesis of \([\text{Ni}\{\text{N}(\text{SPPr}_2)\}_2]\) 40
2.2.3.11 Synthesis of \([\text{Ni}\{\text{N}(\text{SSPPr}_2)\}_2]\) 40
2.2.3.12 Synthesis of \([\text{Ni}\{\text{N}(\text{SSPPr}_2)\}_2]\) 40

2.3 Thin film deposition by CVD 41
2.3.1 Deposition techniques 41
2.3.2 Instrumentation and physical measurements 42
2.3.2.1 Elemental analysis 42
2.3.2.2 Thermogravimetric analysis 42
2.3.2.3 Infrared spectra 42
2.3.2.4 NMR spectroscopy 43
2.3.2.5 Mass spectroscopy 43
2.3.2.6 X-ray diffraction 43
2.3.2.7 Scanning electron microscopy 43
2.4 Results and discussions 44
2.4.1 Infrared 44
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4.2 Single X-ray structure analysis of [Pt{N(SeP\text{Pr}_2)n}]_2</td>
<td>46</td>
</tr>
<tr>
<td>2.4.3 Single X-ray structure analysis of [Pd{N(SPP\text{Ph}_2)n}]_2</td>
<td>51</td>
</tr>
<tr>
<td>2.4.4 The TGA analysis of [Pt{N(SeP\text{Pr}_2)n}]_2</td>
<td>56</td>
</tr>
<tr>
<td>2.4.5 Growth of PtSe\text{sub}_2 thin films from [Pt{N(SeP\text{Pr}_2)n}]_2</td>
<td>56</td>
</tr>
<tr>
<td>2.4.6 The TGA analysis of [Pd{N(Pr_2n\text{Pr}_2)n}]_2</td>
<td>60</td>
</tr>
<tr>
<td>2.4.7 Growth of palladium selenide thin films from [Pd{N(SeP\text{Pr}_2)n}]_2</td>
<td>60</td>
</tr>
<tr>
<td>2.4.8 The TGA analysis of [Pt{N(Pr_2n\text{Pr}_2)n}]_2</td>
<td>65</td>
</tr>
<tr>
<td>2.4.9 Growth of PtS\text{sub}_2 thin films from [Pt{N(Pr_2n\text{Pr}_2)n}]_2</td>
<td>65</td>
</tr>
<tr>
<td>2.4.10 The TGA analysis of [Pd{N(Pr_2n\text{Pr}_2)n}]_2</td>
<td>69</td>
</tr>
<tr>
<td>2.4.11 Growth of Pd_{16}S_{17} thin films from [Pd{N(Pr_2n\text{Pr}_2)n}]_2</td>
<td>69</td>
</tr>
<tr>
<td>2.4.12 The TGA analysis of [Pd{N(Pr_2n\text{Pr}_2)n}]_2</td>
<td>72</td>
</tr>
<tr>
<td>2.4.13 Growth of Pd_{17}Se_{15} thin films from [Pd{N(Pr_2n\text{Pr}_2)n}]_2</td>
<td>72</td>
</tr>
<tr>
<td>2.1.14 The TGA analysis of [Pd{N(Pr_2n\text{Pr}_2)n}]_2</td>
<td>73</td>
</tr>
<tr>
<td>2.4.15 Growth of PdS thin films from [Pd{N(Pr_2n\text{Pr}_2)n}]_2</td>
<td>73</td>
</tr>
<tr>
<td>2.4.16 The TGA analysis of [Pd{N(Pr_2n\text{Pr}_2)n}]_2</td>
<td>74</td>
</tr>
<tr>
<td>2.4.17 Growth of PtSe\text{sub}_2 thin films from [Pt{N(Pr_2n\text{Pr}_2)n}]_2</td>
<td>74</td>
</tr>
<tr>
<td>2.4.18 The TGA analysis of [Pt{N(Pr_2n\text{Pr}_2)n}]_2</td>
<td>77</td>
</tr>
<tr>
<td>2.4.19 Growth of PtS thin films from [Pt{N(Pr_2n\text{Pr}_2)n}]_2</td>
<td>77</td>
</tr>
<tr>
<td>2.4.20 The TGA analysis of [Ni{N(Pr_2n\text{Pr}_2)n}]_2</td>
<td>78</td>
</tr>
<tr>
<td>2.4.21 Growth of NiSe\text{sub}_2 thin films from [Ni{N(Pr_2n\text{Pr}_2)n}]_2</td>
<td>78</td>
</tr>
<tr>
<td>2.4.22 The TGA analysis of [Ni{N(Pr_2n\text{Pr}_2)n}]_2</td>
<td>78</td>
</tr>
<tr>
<td>2.4.23 Growth of NiS\text{sub}_2 thin films from [Ni{N(Pr_2n\text{Pr}_2)n}]_2</td>
<td>78</td>
</tr>
<tr>
<td>2.4.24 The TGA analysis of [Ni{N(Pr_2n\text{Pr}_2)n}]_2</td>
<td>79</td>
</tr>
</tbody>
</table>
CHAPTER 3: Deposition of metal sulphide thin films from xanthate precursors

3.1 Introduction 83

3.2 Experimental 86

3.2.1 Materials and methods 86

3.2.2 Preparation of metal xanthate precursors 86

3.2.2.1 Synthesis of [Ni(S2COR)2], R = Et or iPr 87

3.2.2.2 Synthesis of [Pd(S2COR)2], R = Et or iPr 87

3.2.2.3 Synthesis of [Pt(S2COR)2], R = Et or iPr 88

3.2.2.4 Synthesis of [Cd(S2COR)2], R = Et or iPr 89

3.2.2.5 Synthesis of [Co(S2COR)2], R = Et or iPr 90

3.2.2.6 Synthesis of [Cu(S2C2H5O)2] 90

3.3 Results and discussions 92

3.3.1 Single X-ray structure of [Ni(S2COEt)2] 92

3.3.2 Single X-ray structure of [Pd(S2COEt)2] 95

3.3.3 Single X-ray structure of [Pt(S2COEt)2] 98

3.4 Deposition of metal chalcogenides thin films from

[M(S2COR)2], M = Pt, Pd, Ni, Cd, and Co; R = Et or iPr 101

3.4.1 The TGA analysis of [Ni(S2COR)2], R = Et or iPr 102
3.4.2 Deposition of NiS thin films from [Ni(S₂COR)₂], R = Et or ¹Pr
3.4.3 The TGA analysis of [Cd(S₂COR)₂], R = Et or ¹Pr
3.4.4 Deposition of CdS thin films from [Cd(S₂COR)₂], R = Et or ¹Pr
3.4.5 The TGA analysis [Pd(S₂COCHR₂)₂], R = Et or ¹Pr
3.4.6 Deposition of PdS thin films from [Pd(S₂COR)₂], R = Et or ¹Pr
3.4.7 The TGA analysis of [Pt(S₂COR)₂], R = Et or ¹Pr
3.4.8 Deposition of Pt thin films from [Pt(S₂COR)₂], R = Et or ¹Pr
3.4.9 The TGA analysis of [Co(S₂COR)₂], R = Et or ¹Pr
3.4.10 Deposition of Co₉S₈ thin films from [Co(S₂COR)₂], R = Et or ¹Pr
3.4.11 The TGA analysis of [Cu(C₂H₅OCS₂)₂]
3.4.12 Deposition of CuS thin films from [Cu(S₂C₂H₅O)₂]
3.5 Conclusions

CHAPTER 4: Synthesis of CdS nanoparticles and nanorods

4.1 General introduction
4.2 Optical properties of nanoparticles
4.3 Photoluminescence
4.4 Synthesis of semiconductor nanoparticles using single-molecule precursors
4.5 Shape control of nanoparticles
4.6 General application of nanoparticles
4.6.1 Medical and pharmaceutical
4.6.2 Drug delivery systems
4.6.3 Health monitoring
4.6.4 Disease diagnosis and screening 153
4.6.5 Food processing and storage 153
4.6.6 Energy storage, production and conversion 153
4.6.7 Construction 154
4.6.8 Electronic, optical and magnetic applications 154
4.6.9 Data storage 155
4.6.10 Catalysis 155
4.6.11 Agriculture 155
4.7 Experimental 156
4.7.1 Materials 156
4.7.2 Synthesis of precursors 156
4.7.2.1 Synthesis of \([\text{Cd}(\text{S}_2\text{CNMe}_2)_2]\) 156
4.7.2.2 Synthesis of \([\text{Cd}\{-\text{SC}(-\text{S})\text{OCH(CH}_3\text{)})_2\}_4]\) 157
4.7.3 Preparation of nanoparticles 157
4.7.3.1 Synthesis of CdS Nanoparticles from \([\text{Cd}(\text{S}_2\text{CNMe}_2)_2]\) in tri-n-octylphosphine oxide (TOPO) 157
4.7.3.2 Synthesis of CdS nanoparticles from \([\text{Cd}(\text{S}_2\text{CNMe}_2)_2]\) in hexadecylamine (HDA) 158
4.7.3.3 Synthesis of CdS nanoparticles from \([\text{Cd}\{-\text{SC}(-\text{S})\text{OCH(CH}_3\text{)})_2\}_4]\) in HDA 158
4.8 Results and discussion 159
4.8.1 Synthesis of CdS nanoparticles from \([\text{Cd}(\text{S}_2\text{CNMe}_2)_2]\) in TOPO 159
4.8.1.1 Optical and structural properties 159
4.8.1.2 Structural characteristics 161

4.8.2 Synthesis of CdS nanoparticles from [Cd(S2CNMe2)2] in HDA 163

4.8.2.1 Optical and structural properties 164

4.8.2.2 Structural characteristics 165

4.8.3 Preparation of CdS nanoparticles from [Cd{-SC(=S)OCH(CH3)2}4] in HDA 168

4.8.3.1 Optical and structural properties 168

4.8.3.2 Structural characteristics 169

4.9 Conclusions 172

References 173
### List of tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1.1</td>
<td>Properties of some semiconductors</td>
<td>9</td>
</tr>
<tr>
<td>Table 1.2</td>
<td>Some typical precursors for MOCVD</td>
<td>26</td>
</tr>
<tr>
<td>Table 1.3</td>
<td>Thin films applications</td>
<td>29</td>
</tr>
<tr>
<td>Table 2.1</td>
<td>Infrared spectra (cm⁻¹) of ligands</td>
<td>45</td>
</tr>
<tr>
<td>Table 2.2</td>
<td>Infrared spectra (cm⁻¹) for the precursors</td>
<td>45</td>
</tr>
<tr>
<td>Table 2.3</td>
<td>Crystal data and structural refinement details for [Pt{N(SePr₂)₂}₂]</td>
<td>50</td>
</tr>
<tr>
<td>Table 2.4</td>
<td>Selected bond length (Å) and angles (deg) for [Pt{N(SePr₂)₂}₂]</td>
<td>51</td>
</tr>
<tr>
<td>Table 2.5</td>
<td>Crystal data and structural refinement details for [Pd{N(SPPh₂)₂}₂]</td>
<td>55</td>
</tr>
<tr>
<td>Table 2.6</td>
<td>Selected bond length (Å) and angles (deg) for [Pd{N(SPPh₂)₂}₂]</td>
<td>56</td>
</tr>
<tr>
<td>Table 2.7</td>
<td>XRD data of PtSe₂ thin films</td>
<td>56</td>
</tr>
<tr>
<td>Table 2.8</td>
<td>XRD data of palladium chalcogenide thin films</td>
<td>61</td>
</tr>
<tr>
<td>Table 2.9</td>
<td>XRD data of platinum thin films</td>
<td>66</td>
</tr>
<tr>
<td>Table 2.10</td>
<td>XRD data of PdS₂</td>
<td>69</td>
</tr>
<tr>
<td>Table 2.11</td>
<td>XRD data of PdS thin films</td>
<td>74</td>
</tr>
<tr>
<td>Table 2.12</td>
<td>The TGA data of [M{N(EPR₂)₂}₂], E = S or Se, R = Ph or iPr</td>
<td>80</td>
</tr>
<tr>
<td>Table 3.1</td>
<td>Microanalysis of metal xanthate precursors</td>
<td>91</td>
</tr>
</tbody>
</table>
Table 3.2 Crystal data and structural refinement details for [Ni(S₂COEt₂)₂]

Table 3.3 Selected bond length (Å) and angles (deg) for [Ni(S₂COEt₂)₂]

Table 3.4 Crystal data and structural refinement details for [Pd(S₂COEt₂)₂]

Table 3.5 Selected bond length (Å) and angles (deg) for [Pd(S₂COEt₂)₂]

Table 3.6 Crystal data and structural refinement details for [Pt(S₂COEt₂)₂]

Table 3.7 Selected bond length (Å) and angles (deg) for [Pt(S₂COEt₂)₂]

Table 3.8 X-ray data of NiS (rhombohedral) thin films from [Ni(S₂COR)₂, R = Et or ⁴Pr]

Table 3.9 XRD data of CdS (hexagonal) thin films from [Cd(S₂COR)₂, R = Et or ⁴Pr]

Table 3.10 XRD data of Pd₆S₇ (Cubic) thin films from [Pd(S₂COR)₂, R = Et or ⁴Pr]

Table 3.11 X-ray data of Pt (cubic) thin films from [Pt(S₂COR)₂], R = Et or ⁴Pr

Table 3.12 X-ray data of Co₃S₈ (cubic) thin films from [Co(S₂COR)₂], R = Et or ⁴Pr

Table 3.13 The TGA data of [M(S₂COR)₂], R = Et or ⁴Pr
List of figures

Figure 1.1  Band gap dependence on interatomic spacing 3
Figure 1.2  Fermi-Dirac distributions as a function of temperature 6
Figure 1.3  Schematic diagram of the CVD process 15
Figure 1.4  Apparatus for low pressure metal organic chemical vapour deposition 19
Figure 1.5  Schematic representation of the AACVD process 20
Figure 2.1  Single X-ray structure of [Pt{N(SePr₂)₂}₂] 48
Figure 2.2  Packing diagram of [Pt{N(SePr₂)₂}₂] 49
Figure 2.3  Single X-ray structure of [Pd{N(SPh₂)₂}₂] 53
Figure 2.4  Packing diagram of [Pd{N(SPh₂)₂}₂] 54
Figure 2.5  TGA curve of [Pt{N(SePr₂)₂}₂] 56
Figure 2.6  XRD pattern of PtSe₂ films deposited from [Pt{N(SePr₂)₂}₂] at (a) 400, (b) 425, and 450 °C with Tprec = 225 °C 57
Figure 2.7  SEM images of PtSe₂ films grown at 400 °C, (a) top view, (b) cross view and 450 °C (c) top view (d) cross view 59
Figure 2.8  TGA curve of [Pd{N(SePr₂)₂}₂] 60
Figure 2.9  XRD patterns of Pd₄Se at 475 °C 62
Figure 2.10  XRD patterns of PdSe₂ at 425 °C 62
Figure 2.11  XRD patterns of Pd₁₇Se₁₅ at 450 °C 63
Figure 2.12  SEM images of PdSe₂ films grown at 450 °C, (a) top view, (b) Cross view and 475 °C, (c) top view 64
Figure 2.13  TGA curve of [Pt\{N(SPPrzh}_{2}\}_{2}] 65
Figure 2.14 XRD pattern of Pt film deposited from [Pt\{N(SPPrzh}_{2}\}_{2}] 66
Figure 2.15 SEM micrographs of Pt thin films from [Pt\{N(SPPrzh}_{2}\}_{2}]
at 450 °C, (a) top view, (b) Cross view 68
Figure 2.16 XRD pattern of PdS$_2$ thin film deposited from
[Pd\{N(SPPrzh}_{2}\}_{2}] 70
Figure 2.17 SEM micrographs of PdS$_2$ thin film from [Pd\{N(SPPrzh}_{2}\}_{2}]
at 500 °C, (a) top view, (b) Cross view 71
Figure 2.18 XRD of Pd$_7$Se$_{15}$ from [Pd\{N(SePPhzh}_{2}\}_{2}] 72
Figure 2.19 XRD pattern of PdS thin films deposited [Pd\{N(SePPhzh}_{2}\}_{2}] 73
Figure 2.20 XRD pattern of PtSe$_2$ from [Pt\{N(SePPhzh}_{2}\}_{2}] 75
Figure 2.21 SEM micrographs of PtSe$_2$ thin film from [Pt\{N(SePPhzh}_{2}\}_{2}]
(a) & (c) top view, (b) & (d) Cross view 76
Figure 2.22 XRD pattern of Pt thin film deposited from
[Pt\{N(SPPPhzh}_{2}\}_{2}] 77
Figure 3.1 ORTEP diagram showing atomic numbering of
[Ni(SzCOEtzh}_{2}] 92
Figure 3.2 Packing diagram of [Ni(SzCOEtzh}_{2}] 92
Figure 3.3 ORTEP diagram showing atomic numbering of
[Pd(SzCOEtzh}_{2}] 96
Figure 3.4 Packing diagram of [Pd(SzCOEtzh}_{2}] 96
Figure 3.5 ORTEP diagram showing atomic numbering of
[Pt(SzCOEtzh}_{2}] 99
Figure 3.6  Packing diagram of \([\text{Pt}(\text{S}_2\text{COEt})_2] \)

Figure 3.7  TGA curve of \([\text{Ni}(\text{C}_2\text{H}_5\text{OCS})_2] \)

Figure 3.8  TGA curve of \([\text{Ni}(\text{C}_3\text{H}_7\text{OCS})_2] \)

Figure 3.9  XRD pattern of NiS from \([\text{Ni}(\text{C}_2\text{H}_5\text{OCS})_2] \) at 200 °C

Figure 3.10  XRD pattern of NiS from \([\text{Ni}(\text{C}_2\text{H}_5\text{OCS})_2] \) at 250 °C

Figure 3.11  XRD pattern of NiS from \([\text{Ni}(\text{C}_2\text{H}_5\text{OCS})_2] \) at 300 °C

Figure 3.12  XRD pattern of NiS from \([\text{Ni}(\text{C}_3\text{H}_7\text{OCS})_2] \) at 200 °C

Figure 3.13  XRD pattern of NiS from \([\text{Ni}(\text{C}_3\text{H}_7\text{OCS})_2] \) at 250 °C

Figure 3.14  XRD pattern of NiS from \([\text{Ni}(\text{C}_3\text{H}_7\text{OCS})_2] \) at 300 °C

Figure 3.15  SEM micrographs of NiS from \([\text{Ni}(\text{C}_2\text{H}_5\text{OCS})_2] \)

at 200 °C

Figure 3.16  SEM micrographs of NiS from \([\text{Ni}(\text{C}_2\text{H}_5\text{OCS})_2] \)

at 250 °C

Figure 3.17  SEM micrographs of NiS from \([\text{Ni}(\text{C}_2\text{H}_5\text{OCS})_2] \)

at 300 °C

Figure 3.18  XRD pattern of NiS from \([\text{Ni}(\text{C}_3\text{H}_7\text{OCS})_2] \)

at (a) 200 °C, (b) 250 °C, and (c) 300 °C

Figure 3.19  XRD pattern of CdS from \([\text{Cd}(\text{C}_2\text{H}_5\text{OCS})_2] \) at 200 °C

Figure 3.20  XRD pattern of CdS from \([\text{Cd}(\text{C}_2\text{H}_5\text{OCS})_2] \) at 250 °C

Figure 3.21  XRD pattern of CdS from \([\text{Cd}(\text{C}_2\text{H}_5\text{OCS})_2] \) at 300 °C

Figure 3.22  XRD pattern of CdS from \([\text{Cd}(\text{C}_3\text{H}_7\text{OCS})_2] \) at 200 °C

Figure 3.23  XRD pattern of CdS from \([\text{Cd}(\text{C}_3\text{H}_7\text{OCS})_2] \) at 250 °C

Figure 3.24  XRD pattern of CdS from \([\text{Cd}(\text{C}_3\text{H}_7\text{OCS})_2] \) at 300 °C
Figure 3.25  SEM micrographs of CdS from [Cd(C$_2$H$_5$OCS$_2$)$_2$] at 200 °C

Figure 3.26  SEM micrographs of CdS from [Cd(C$_2$H$_5$OCS$_2$)$_2$] at 250 °C

Figure 3.27  SEM micrographs of CdS from [Cd(C$_2$H$_5$OCS$_2$)$_2$] at 300 °C

Figure 3.28  XRD pattern of CdS from [Cd(C$_2$H$_5$OCS$_2$)$_2$] at
(a) 200 °C (b) 250 °C, and (c) 300 °C

Figure 3.29  XRD pattern of Pd$_{16}$S$_7$ from [Pd(C$_2$H$_5$OCS$_2$)$_2$] at 200 °C

Figure 3.30  XRD pattern of Pd$_{16}$S$_7$ from [Pd(C$_2$H$_5$OCS$_2$)$_2$] at 250 °C

Figure 3.31  XRD pattern of Pd$_{16}$S$_7$ from [Pd(C$_2$H$_5$OCS$_2$)$_2$] at 300 °C

Figure 3.32  SEM micrographs of PdS from [Pd(C$_2$H$_5$OCS$_2$)$_2$] at 250 °C

Figure 3.33  SEM micrographs of PdS from [Pd(C$_2$H$_5$OCS$_2$)$_2$] at 300 °C

Figure 3.34  XRD pattern of Pt thin films from [Pt(C$_2$H$_5$OCS$_2$)$_2$] at 200 °C

Figure 3.35  XRD pattern of Pt thin films from [Pt(C$_2$H$_5$OCS$_2$)$_2$] at 250 °C
Figure 3.36  XRD pattern of Pt thin films from [Pt(C₂H₅OCS₂)₂]
at 300 °C 128

Figure 3.37  XRD pattern of Co₉S₈ thin films from [Co(C₂H₅OCS₂)₂]
at 200 °C 130

Figure 3.38  XRD pattern of Co₉S₈ thin films from [Co(C₂H₅OCS₂)₂]
at 250 °C 131

Figure 3.39  XRD pattern of Co₉S₈ thin films from [Co(C₂H₅OCS₂)₂]
at 300 °C 131

Figure 3.40  SEM micrographs of Co₉S₈ from [Co(C₂H₅OCS₂)₂]
at 200 °C 133

Figure 3.41  SEM micrographs of Co₉S₈ from [Co(C₂H₅OCS₂)₂]
at 250 °C 134

Figure 3.42  SEM micrographs of Co₉S₈ from [Co(C₂H₅OCS₂)₂]
at 300 °C 135

Figure 4.1  Excitation across the band gap by photon absorption:
(a) direct process; (b) indirect process 142

Figure 4.2  Single-source approach for preparing semiconductor
nanocrystallites in TOPO 146

Figure 4.3  TGA curve of [Cd(S₂CNMe₂)₂] 159

Figure 4.4  Optical absorption spectra of CdS nanoparticles 160

Figure 4.5  XRD pattern of TOPO capped CdS nanoparticles from
[Cd(S₂CNMe₂)₂] 161

Figure 4.6  TEM images of CdS nanoparticles capped by TOPO 163
Figure 4.7  Optical absorption spectra of CdS nanoparticles 164
Figure 4.8  PL spectra of HDA capped CdS nanoparticles 165
Figure 4.9  XRD pattern of CdS nanoparticles from [Cd(S_2CNMe_2)_2] in HDA 166
Figure 4.10  TEM images of HDA capped CdS nanorods from [Cd(S_2CNMe_2)_2] 167
Figure 4.11  TGA curve of [Cd{-SC(=S)OCH(CH_3)z}_4] 168
Figure 4.12  Optical absorption spectra of CdS nanoparticles from [Cd{-SC(=S)OCH(CH_3)z}_4] 169
Figure 4.13  XRD pattern of CdS nanoparticles from [Cd{-SC(=S)OCH(CH_3)z}_4] 170
Figure 4.14  TEM images of HDA capped CdS nanorods from [Cd{-SC(=S)OCH(CH_3)z}_4] 171
**List of abbreviations and symbols chemicals**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Chemical Name</th>
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<tbody>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>THF</td>
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<td>R</td>
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<td>Et</td>
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<td>Methyl group</td>
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<tr>
<td>`Bu</td>
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</tr>
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<td>E</td>
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<td>TOPO</td>
<td>Tri-n-octylphosphine oxide</td>
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<td>NaOMe</td>
<td>Sodium methoxide</td>
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<td>M</td>
<td>Transition metal</td>
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### Ligands and precursors prepared in this project

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<td>NH(Se^tPr_2)_2</td>
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<td>Iminobis(diisopropylseleniumphosphine)</td>
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<td>NH(SP^tPr_2)_2</td>
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<td>[Cd(S_2CO Et)_2]</td>
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\[
\begin{align*}
[Cd(S_2CO\textsuperscript{i}Pr)_2] & \quad [\text{Bis(isopropylxanthato)cadmium(II)}] \\
[Co(S_2CO\textsuperscript{Et})_2] & \quad [\text{Bis(ethylxanthato)cobalt(III)}] \\
[Co(S_2CO\textsuperscript{i}Pr)_2] & \quad [\text{Bis(isopropylxanthato)cobalt(III)}] \\
[Cu(S_2\textsuperscript{Et})_2] & \quad [\text{Bis(ethylxanthato)copper(II)}] \\
[Cd(S_2\text{CNMe}_2)_2] & \quad [\text{Tetramethyldithiocarbamates cadmium(II)}] \\
[Cd\{SC(=S)OCH(CH_3)\}_4] & \quad [\text{Bis(isopropylxanthatodisulfide)cadmium(II)}]
\end{align*}
\]

**Techniques and Methods**

- **NMR**: Nuclear magnetic resonance
- **MS**: Mass Spectrometer
- **FT-IR**: Fourier Transform Infrared
- **UV-Vis**: Ultraviolet visible spectroscopy
- **PL**: Photoluminescence
- **TGA**: Thermogravimetric analysis
- **CVD**: Chemical vapour deposition
- **AACVD**: Aerosol assisted chemical vapour deposition
- **LP-MOCVD**: Low pressure metal organic chemical vapour deposition
- **MBE**: Molecular beam epitaxy
- **ALD**: Atomic layer deposition
- **XRD**: X-ray diffraction
- **SEM**: Scanning electron microscopy
- **TEM**: Transmission electron microscopy
- **EDAX**: Energy dispersive X-ray analysis
MO  Molecular orbitals
LCAO  Linear combination of atomic orbital

Symbols and Constants

a.u.  Arbitrary units
α  Absorption coefficient
E  Energy
M  Mobility
T  Temperature
λ  Wavelength
K  Wave vector
K_{sp}  Solubility product
Σ  Conductivity
E_{f}  Fermi energy
B  Magnetic field
λ_{exc}  Excitation wavelength (Luminescence)
ε  Dielectric coefficient
min  Minutes
h  Hour
t  Time
R  Radius
D  Diameter
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>E</td>
<td>Elementary charge</td>
</tr>
<tr>
<td>a_B</td>
<td>Bohr radius</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>C</td>
<td>Celcius</td>
</tr>
<tr>
<td>E_g</td>
<td>Band gap energy</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>Λ</td>
<td>Wavelength</td>
</tr>
<tr>
<td>S</td>
<td>Singlet</td>
</tr>
<tr>
<td>d</td>
<td>Doublet</td>
</tr>
<tr>
<td>m</td>
<td>Multiplet</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volt</td>
</tr>
<tr>
<td>MHz</td>
<td>Megahertz</td>
</tr>
<tr>
<td>ORTEP</td>
<td>Oak ridge thermal ellipsoid plot</td>
</tr>
<tr>
<td>Ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>Sccm</td>
<td>Standard cubic centimeters per minute</td>
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</table>
Acknowledgements

At the outset, I would like to express my appreciation to Professor Neerish Revaprasadu and Professor G.A Kolawole for their advice during my doctoral research endeavor for the past three years. Their observations and comments helped me to establish the overall direction of the research and to move forward with investigation in depth. I am grateful to numerous local and global “peers” who have contributed towards shaping this thesis. I am much in debt to Professor P. O’Brien for giving me an opportunity to visit his laboratory at the University of Manchester to work with a talented team of researchers. Many thanks again to him for answering what seemed to be unanswerable questions and supplying desperately needed assistance and suggestions during my visit.

In addition, I would like to acknowledge Mike Faulkner from University of Manchester for technical assistance with all SEM reported in this dissertation. I would also like to thank Keith Pell from Queen Mary College in London for the TEM measurements. I would also like to thank Dr. P. Christian for providing assistance in general laboratory matters and for providing useful insight regarding my research project. I would like to send my gratitude to my research colleagues at University of Zululand, Peter, Justice, Chilli, Sosibo, and Sibusiso for their support and friendship.

I also gratefully acknowledge the National Research Foundation (South Africa), the Royal Society (UK) for the financial support. I would also like to thank University of Zululand for giving me an opportunity to further my studies and University of Manchester for allowing me to use their facilities during my visit.
Lastly, and most importantly, I wish to thank my family, my wife Elelwani, my daughter Masindi and my three sons Thendo, Khuthadzo and Khumbudzo for their love, endless patience, and understanding—they allowed me to spend most of the time on this thesis. My parents, Thifulufhelwi and Thinavhuyo Musetha have been an inspiration throughout my life. They bore, raised, supported, taught, and loved me throughout all my years. I’d like to thank them for all they have done for me. I’d like to thank Prof. Sandile Songca for encouraging me to finish my PhD. My best friend Gumani Mudau for being there for me during difficult times and transporting my kids to school when I was in Durban finalizing my PhD thesis. And finally but most importantly I would like to thank God for His Love and guidance.
DEDICATION

This work is dedicated to my wife, parents and to the memory of my late sister, Khathutshele Musetha and late friend, Jim Chapman.
Chapter 1

General introduction to semiconductor thin films
1.1 Background

Semiconductor materials are distinguished by having their specific electrical conductivity between that of conductors and insulators. Materials act as semiconductors due to the nature of the chemical bonding within the material and the resulting configuration of the electrons associated with this bonding character. Both silicon and germanium have electronic structures with four valence electrons available for bonding, silicon having the configuration [Ne]3s²3p². Although there are many techniques available for preparing semi-conducting thin films, it is generally difficult to maintain the stoichiometry of the materials.¹-⁴

1.2 Band theory

In general, for most semiconductor and insulators, conductivity (σ) increases rapidly with temperature, whereas for metals, there is a gradual decrease in conductivity with increasing temperature. The electronic properties of solid materials can be described by band theory. In the present study, only a brief outline of the important conclusions of the band theory will be given. In simplified terms, the basis for band theory originates from the behaviour of the atomic orbital in infinite structures, where there is overlap between the atomic orbitals to lead into the formation of continuous bands.
The electronic properties of a solid depend on the nature of these bands, their width, the number of electrons they can hold and the number of electrons in the entire system (hence "quantum dots" of semiconductors have different band structure from the bulk material). The width of the bands depends on the degree of overlap of the respective orbital. Weakly interacting orbitals lead to narrow bands whereas strongly interacting orbitals lead to wide bands. The electrons in a wide band are considered to be dispersed over the entire lattice, whereas electrons in a narrow band are more associated with the nuclei. The differences between metals, semiconductors and insulators depend largely on their respective band structures and the magnitude of any energy gap between full and empty bands.

The qualitative diagrams employed in band theory are derived differently by chemists and physicists/material scientists. The chemist's approach is to take the orbital of each atom, apply a linear combination of atomic orbital (LCAO) approximation and extend to the level of an infinite 3-dimensional structure. By contrast, the physicists use a
free-electron model that ignores the orbital of each atom and instead builds up the electronic bands using only the wave functions of the electrons. The chemists approach to band theory, therefore, is to extend molecular orbital (MO) theory to infinite three-dimensional structures. In diatomic molecules, an atomic orbital from one atom overlaps with an atomic orbital from the second atom to produce two molecular orbitals, which are delocalized over both atoms. One of the MOs represents a bonding orbital of lower energy than the atomic orbital; the other MO forms an antibonding orbital of higher energy than the atomic orbital. For increasingly large molecular clusters the number of MOs increases, consequently the average energy gap between adjacent orbitals is reduced. Hence the energy gap between electronic levels in the bonding and antibonding orbitals diminishes until a continuum of energy levels is obtained. In contrast, the free electron model used by physicists postulates that band gaps are derived from the interaction of free electrons with the changes in periodic potential through the crystal lattice. Qualitatively the two models produce very similar band diagrams in 2- or 3-dimensions, differences are apparent, however, in 1-D.

The energy corresponding to the highest filled electronic state at 0 K is called the Fermi energy, $E_F$. Figure 1.1a represents the electron band structure found for many transition metals, where the outermost band is only partially filled with electrons, whereby the electrons can move freely. Each transition metal atom has one 4s electron, hence in the solid, comprised of $N$ atoms, the 4s band can accommodate $2N$ electrons so the band is half filled, facilitating electron conduction. The electron band structure of metals such as magnesium, where there is an overlap of empty and filled bands, is shown in Figure 1.1b. However, when a solid is formed there is overlap of the 3s and 3p bands. The band structure for insulators and semiconductors are similar.
in the sense that one band is completely filled (valence band) and the others are empty (conduction band). The difference between the two structures lies in the magnitude of the band gap $E_g$. For insulators the band gap is relatively wide (generally $> 4 \text{ eV}$), whereas for semiconductors it is smaller ($< 4 \text{ eV}$). The Fermi level for the latter band structures lies within the "forbidden gap" between the valence and the conduction edges. In the presence of an electric field, only electrons with energies greater than the Fermi energy are acted upon and participate in the conduction process. These electrons are called free electrons. For semiconductors and insulators, electron states in the valence band can only become available if electrons are promoted across the energy band gap into the conduction band. This can only be achieved if the electrons are supplied with a minimum energy equal to the band gap energy and are usually accomplished with an external non-electrical source such as light or heat.

Figure 1.2 shows the excitation process and the implications of Fermi function for the electrical conductivity of a semiconductor. At higher temperatures, a larger fraction of the electron can bridge this gap and participate in the electrical conduction. Increasing the temperature leads to an increase in the number of carriers and a corresponding increase in conductivity.
Figure 1.2 Fermi-Dirac distributions as a function of temperature

At low temperatures, the valence band is completely full, making the material an insulator. For every electron excited into the conduction band, a vacant electron state, known as a positive hole, is left in the valence band. The number of electrons excited thermally depends on both the band gap and the temperature. At a given temperature, the larger the band gap, the lower the probability that an electron may be promoted to the conduction band. Increasing the temperature results in greater thermal energy for electron excitation and therefore enhances the conductivity. 1-6

1.3 Theory of semiconductors

Since the introduction of the transistor in the 1950s and the development of the integrated silicon chip in the 1970s, semiconductor based devices have been increasingly impinging on our everyday lives. The trend is likely to continue, with increasing demand for new, technologically advanced consumer products such as
General introduction to semiconductor thin films

mobile cell phones and laptop computers. Although silicon-based technology is by far the most advanced amongst semiconductor technology, there is increasing interest in use of compound semiconductors (e.g. GaAs, ZnO etc.) that possess electrical and optical properties that are absent in silicon. One of the main reasons that semiconductors are useful in electronic devices is that their electronic properties can be greatly altered in a controllable way by adding small amount of impurities.

The conductivities are particularly sensitive to the variations in temperature, impurities and light. Generally the conductivity of semiconductors is given by equation 1.1,

\[ \alpha = ne\mu \]  

**eq. 1.1**

where \( n \) is the carrier concentration (the concentration of carriers per \( \text{cm}^3 \)), \( e \) is the charge on the carriers and \( \mu \) is their mobility (the ratio of the drift velocity and the electric field).

The temperature-dependence of the bandgap energy can be determined with the following expression for \( E_g \) as a function of the temperature \( T \):

\[ E_g(T) = E_g(0) - \alpha T^2/T + \beta \]  

**eq. 1.2**

where \( E_g(0) \), \( \alpha \), and \( \beta \) are the fitting parameters.

This conductivity is due to the generation of charge carriers which are thermally excited. In contrast, the conductivity of a metal decreases at higher temperatures due to electron-phonon collisions. Dopants are introduced in order to enhance the conducting potential of a semiconductor. The quantity of the dopant is not the only factor that can limit the electrical properties of the semiconductor, the type of
impurity is also particularly important. Another limiting factor is due to defects found in the crystal lattice. These impurities can either be unintentional due to lack of control during the growth of the semiconductor or they can be added deliberately to provide mobile current carriers in the semiconductor. Semiconductors can be divided into two types, intrinsic and extrinsic. Semiconductors that rely on temperature to conduct charge or emit light are called intrinsic semiconductors. However, the presence of impurities in the material will generate extra carriers at a much higher concentration than those that are generated thermally in the intrinsic semiconductor. These 'doped' semiconductors are called extrinsic semiconductors. They contain impurities (or foreign atoms) incorporated into the crystal structure of the semiconductor. High impurities concentration has detrimental effects on the electrical quality of the material. In many devices the intrinsic conductivity is undesirable, and larger band gap materials give better performance. The band gaps of some compound are given in Table 1.1.
Table 1.1 Properties of some semiconductors

<table>
<thead>
<tr>
<th>Materials</th>
<th>Groups</th>
<th>Band Gaps/eV</th>
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<tbody>
<tr>
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<td>1.43</td>
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<tr>
<td>GaN</td>
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<td>GaSb</td>
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<tr>
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</tr>
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<tr>
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<tr>
<td>PbTe</td>
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<td>0.31</td>
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</table>

1.4 Deposition of Semiconductor Thin Films

There are a number of methods by which semi conducting material can be deposited on substrates. These methods can be divided into two groups; i.e. chemical and physical techniques.

1.4.1 Thin Film Deposition Techniques

There are many vapour phase deposition/growth techniques available. Most important of these are chemical vapour deposition (CVD), vapour phase epitaxy (VPE) and physical vapour deposition (PVD) techniques. The techniques are based in the
formation of vapour of the material to be deposited, so that the vapour is condensed on the substrate surface as a thin film. Usually the process must be performed in vacuum or in controlled atmosphere, to avoid interaction between vapour and air.

Chemical vapour deposition or CVD is a generic name for a group of processes that involve depositing a solid material from a gaseous phase and is similar in some respects to physical vapour deposition (PVD). A range of other techniques are available for the deposition of semiconductor thin films, namely evaporation, sputtering, metal-organic chemical vapour deposition (MOCVD), aerosol-assisted chemical vapour deposition (AACVD), atomic layer deposition (ALD) and molecular beam epitaxy (MBE). Each technique has intrinsic strengths and weaknesses, as well as specific advantages for specific applications.

Volatility of compounds is a prerequisite for deposition in the conventional CVD. It is a function of intermolecular forces (van der Waals interaction, pi-stacking or hydrogen bonds) which are affected by molecular weight, geometry and, for solids, lattice structure. Several CVD techniques have been employed for the growth of a variety of materials in this work, including low pressure metal-organic chemical vapour deposition (LP-MOCVD) and AACVD.

1.4.2 Physical Vapour Deposition or Vacuum Deposition Techniques

PVD can be divided into two processes, evaporation and sputtering.
1.4.2.1 Physical Vapour Deposition (PVD) by Evaporation

During evaporation the material being deposited is heated under ultra high vacuum to vaporise the species which condense on the substrate surface. The base pressure in the reaction chamber is generally lower than $10^{-7}$ Torr, where the mean free path of the evaporated species is enough to allow it to condense on the substrate surface without collisions with residual gas molecules. However, deposition of alloy films using an evaporation technique is somewhat difficult because of differences in vapour pressures of the various elements, e.g. the growth of alloys containing both As and P.

PVD differs in that the precursors are solid, with the material to be deposited being vaporised from a solid target and deposited onto the substrate.

1.4.2.2 Physical Vapour Deposition (PVD) by Sputtering

Sputtering is the deposition of particles vaporised from surface, which is called the "sputtering target", by the physical sputtering process. Physical sputtering is a non-thermal vaporization process. Surface atoms are physically ejected by momentum transfer from an energetic bombarding particle which is usually a gaseous ion accelerated from plasma. Sputtering deposition can be performed in high vacuum or low pressure where the sputtered particles do not suffer gas phase collisions in the space between the target and the substrate.

There are several advantages of using sputtering deposition. Unlike vacuum evaporation, alloy films can be produced by sputtering deposition due to the target providing a stable, long-lived vaporisation source. The second advantage is that in
some configurations, reactive deposition can be easily accomplished using reactive
gaseous species that are activated in plasma.\textsuperscript{16-17}

\subsection*{1.4.3 Chemical Vapour Deposition (CVD)}

The family of CVD techniques is the most flexible method to create nanostructures
today. With many forms of CVD existing, it can be used efficiently toward many
applications. The CVD technique has been used for many years in the semiconductor
industry to thin film deposition (epitaxy) on substrates. In a traditional sense, CVD is
used to create layers of semiconductors, insulators, or conductors in a sort of ‘sand
wich’ of layers. CVD has been proved to be a useful method for the deposition of thin
films for many applications. The CVD techniques are a vapour deposition technique
based on homogeneous or heterogeneous chemical reactions. Depending on
conditions such as vapour pressure and temperature, both types of reaction or only
one of them, takes place during deposition process. These processes employ various
gaseous, liquid and solid chemical as sources of elements (precursors) of which the
film is to be formed. A large variety of single crystalline, polycrystalline and
amorphous thin films of metals have been formed. Dielectrics and semiconductors of
III-V and II-VI groups were prepared by the CVD technique.\textsuperscript{18-19} The factors affecting
uniformity of surface morphology are from a variety of sources, depending on
whether the vacuum or fluid are enough to support mass transport (e.g. if mass
transport is not enough, it can result in a non uniform surface morphology over the
substrate surface area). The third step is the actual deposition of the film on the
substrate surface where adsorption occurs. Deposition behaviour is determined by the
source and transport factors and by conditions at the deposition surface. There are
three principal factors which determine the deposition behaviour on the surface, the
General introduction to semiconductor thin films

substrate surface condition, the reactivity of the arriving material, and the energy input. 18-20

The Process Steps for Thin film Deposition

Precursor gases (often diluted in carrier gases) are delivered into the reaction chamber at approximately ambient temperatures. As they pass over or come into contact with a heated substrate, they react or decompose forming a solid phase, which are deposited onto the substrate. The substrate temperature is critical and can influence what reactions take place.

A CVD apparatus consists of several basic components:

* Gas delivery system – For the supply of precursors to the reactor chamber.
* Reactor chamber – Chamber within which deposition takes place.
* Substrate loading mechanism – A system for introducing and removing substrates, mandrels c.t.c.
* Energy source – Provides the energy/heat that is required to get the precursors to react/decompose.
* Vacuum system – A system for removal of all other gaseous species other than those required for the reaction/deposition.
* Exhaust system – System for removal of volatile by-products from the reaction chamber.
* Exhaust treatment systems – In some instances, exhaust gases may not be suitable for release into the atmosphere and may require treatment or conversion to safe/harmless compounds.
General introduction to semiconductor thin films

- Process control equipment – Gauges, controls etc to monitor process parameters such as pressure, temperature and time.

- Energy Sources

There are several suitable sources of heat for CVD processes. These include:

- Resistive heating e.g. tube furnaces
- Radiant heating e.g. halogen lamps
- Radio frequency heating e.g. induction heating
- Lasers: or lasers as a source of photo energy.

Other energy sources may include UV-Visible light.

The condition of the substrate surface includes roughness, level of contamination, degree of chemical bonding with the formed materials, and crystallographic parameters, in the case of epitaxy. The second factor is the reactivity which refers to the probability of arriving molecules reacting with the surface and becoming incorporated into the film. Finally the third factor is the energy input to the surface. Growth temperature (substrate temperature) is the basic source of energy input.

A schematic representation of a CVD process is illustrated in Figure 1.3
A volatile precursor is transported to the substrate in the reactor by a carrier gas (1). At the substrate, the precursor sorbs (2) and reacts (3) to liberate the by products that subsequently desorbs (6) and transported out of the reactor (7). The target atoms then diffuse (4) to form nuclei of the materials (e.g. PtSe$_2$), where subsequent growth occurs (5).

1.4.3.1 Metal-organic Chemical Vapour Deposition (MOCVD)

One form of CVD, known as MOCVD, offers various advantages over the traditional process. The use of organometallic compounds means that lower temperatures can be used for the deposition process which saves time, energy and costs. MOCVD is a technique for growing solid films on a substrate by gas-phase and surface reactions; it is a relatively new process, pioneered in 1981 by Manasevit.\textsuperscript{21}
MOCVD reactors are generally operated at intermediate pressures (e.g. 1-200 mbar) so that chemical reactions occur both in the gas phase and on, or close to, the substrate. MOCVD offers the potential for large area growth, and has the advantages of good composition control, high film uniformity, and good doping control and most importantly, it gives excellent conformational step coverage on non-planar device geometries. An essential requirement for a successful MOCVD process is the availability of precursors with the appropriate properties and decomposition characteristics. For instance, the precursor must have an adequate temperature window between precursor evaporation and decomposition, and for many electronic applications.

MOCVD relies on the volatility of the precursor material, such that it would sublime into the vapour phase (without first decomposing) and then react over a heated substrate, decomposing to deposit a solid species, for example (equation 1.3), a metal sulphide thin film. The process proceeds under non-equilibrium conditions by generating chemically active species which induce the growth of the solid network. At the centre of this deposition process is the parent, or carrier gas containing the element(s) required as the film constituent(s).

\[ \text{Me}_3\text{In} + \text{H}_2\text{S} \rightarrow \text{In}_x\text{S}_y + \text{by-products} \quad \text{eq. 1.3} \]

The goal of modern MOCVD is to provide films with the following characteristics:

- Good thickness uniformity
- Controlled composition and stoichiometry
- High purity and density
General introduction to semiconductor thin films

- Good adhesion to substrate
- A high degree of structural perfection
- Good mechanical, optical and electrical properties

To achieve these goals, reactor design is important. In conventional MOCVD (atmospheric pressure), a carrier gas is bubbled through the liquid and/or solid precursors, and assuming that the compound exhibits its equilibrium vapour pressure, the precursors are carried into the reactor. The chemical reactions that occur in the gas phase determine the composition and structure of the solid film.

The MOCVD process offers a very flexible approach to the decomposition of metal oxide thin films, and has the advantage of rapid deposition for covering large areas of the substrate. In addition, stoichiometry, morphology, and even crystal structure and orientation can be tailored by controlling the deposition parameters. Also, since unlike other techniques, MOCVD does not require line of sight with the vapour source, it has excellent conformal step coverage at device dimensions over 2μ, which is particularly important in micro-electronic applications.

The principal disadvantages of conventional MOCVD are the nonavailability of suitable precursors with sufficient volatility and stability, as well as adequate purity and the need to obtain high vapour pressures of sometimes-hazardous precursors. It is also difficult to completely rule out the unwanted vapour phase reactions between the metal precursors and gases above the substrate, which presumably generate undesirably large mixed metal intermediates and oxide complexes. In conventional MOCVD the precursors are typically highly volatile materials such as metal alkyls, or
General introduction to semiconductor thin films

Hydrides such as arsine or hydrogen selenide. These compounds have several disadvantages, the alkyls are highly pyrophoric, and the majority of the hydrides are gases of considerable toxicity. Therefore, there have been considerable efforts directed towards the development of alternate precursors for conventional MOCVD, e.g. by forming adducts of the parent alkyls.

A number of modified MOCVD techniques have been used to overcome the problems associated with conventional MOCVD. However, MOCVD offers significant advantages over physical vapour deposition (PVD) method, in many aspects, simple apparatus, mild process conditions, control over composition (excellent composition control), high deposition rates (deposition capability), and possible large scale processing, film uniformity.22-36

LP-MOCVD is an attractive technique. In general, most reactions involving hazardous toxic vapour phase precursors are undertaken at reduced pressure from safety perspective. Additionally, the enhancement of kinetic steps often occurs at reduced pressure in the chemical deposition system.
This approach depends on the sublimation of the precursors with or without a carrier gas. If the vapour pressure of the precursor is high enough to rely on the carrier gas, for example, WF₆ has a vapour pressure of 1000 Torr at 25 °C, and thus the precursor can be used without carrier gas and feed rate limitations usually do not occur. A number of II/VI and III/VI semiconductor materials have been deposited using this technique.37-62

1.4.3.2 Aerosol-Assisted Chemical Vapour Deposition (AACVD)

In AACVD an aerosol is injected directly into a vapourising chamber where the precursor and solution evaporate. In contrast, LP-MOCVD and/or convectional CVD rely on the delivery of the precursor at its equilibrium vapour pressure at the source.
temperature. In general, aerosol delivery systems are suitable techniques where the precursor is thermally sensitive and slowly decompose if heated for extended periods of time needed to elevate the vapour pressure. It is also a useful method for multicomponent systems as several precursors can be dissolved in the same solution and the relative delivery rates of precursors are defined by composition. The AACVD process is illustrated in Figure 1.5.

![Figure 1.5 Schematic representation of the AACVD process](image)

A single source precursor is dissolved in an organic solvent (1) and is converted into droplets by a piezoelectric modulator (2). The aerosol of precursor and solvent is then transported by a carrier gas into a hot zone where it evaporates. The vapour of the precursor is then transported to the substrate where it evaporates. The vapour of the precursor is then transported to the substrate where it adsorbs and reacts to form a film and by-products (3) and (4). AACVD is an example of a family of assisted CVD techniques, liquid injection CVD and spray pyrolysis.\textsuperscript{63-81}
1.4.4 Atomic layer deposition (ALD)

ALD is a modification of MOCVD, in which gaseous precursors are successively introduced to the substrate surface in a repeated cycle. Between the cycles, the volatile reaction products are flushed from the reactor by purging with an inert gas or by evacuation. ALD process has a self-limiting mechanism in which the growth surface becomes saturated with precursor or reactant molecules, so that film growth automatically stops (or ‘self-limits’) at one or sometimes two monolayer. Under these conditions the film growth rate becomes independent of the precursor pulse length. ALD relies on the surface exchange reactions between chemisorbed metal-containing precursor fragments and adsorbed nucleophilic reactant molecules. The surface-controlled growth in ALD leads to highly uniform coverage (or conformality) of planar substrates, as well as non-planar surface containing trenches or vias, and high surface area (high aspect ratio geometries) substrates such as silica and alumina powders. The precursor must have favourable stereochemistry for rapid reaction with adsorbed nucleophilic reactants, leading to a facile and clean elimination of its ligands. 82-84

1.4.5 Molecular beam epitaxy (MBE)

Molecular beam epitaxy (MBE) was developed in the early 1970s as a means of growing high-purity epitaxial layers of compound semiconductors. Since that time it has evolved into a popular technique for growing III-V compound semiconductors as well as several other materials. MBE can produce high-quality layers with very abrupt interfaces and good control of thickness, doping, and composition. Because of the high degree of control possible with MBE, it is a valuable tool in the development of
sophisticated electronic and optoelectronic devices.

In MBE, the constituent elements of a semiconductor in the form of 'molecular beams' are deposited onto a heated crystalline substrate to form thin epitaxial layers. The 'molecular beams' are typically from thermally evaporated elemental sources, but other sources include metal-organic group III precursors metalorganic molecular beam epitaxy (MOMBE), gaseous group V hydride or organic precursors (gas-source MBE), or some combination (chemical beam epitaxy or CBE). To obtain high-purity layers, it is critical that the material sources be extremely pure and that the entire process be done in an ultra-high vacuum environment. Another important feature is that growth rates are typically on the order of a few Å/s and the beams can be shuttered in a fraction of a second, allowing for nearly atomically abrupt transitions from one material to another.

MBE is a method of laying down layers of materials with atomic thicknesses on to substrates. This is done by creating a 'molecular beam' of a material which impinges on to the substrate. The resulting 'super lattices' have a number of technologically important uses including quantum well lasers for semi conducting systems, and giant magneto-resistance for metallic systems.

1.5 Precursors for Semiconductor Thin Films

In the preparation of thin film semiconductor materials, a principal concern is the choice of precursor to deliver the necessary constituent atoms to the substrate. The precursor used for thin film deposition can be a solid, liquid, vapour or gas. In the transport step, the most important factor is uniformity over the substrate area.
General introduction to semiconductor thin films

The composition and microstructure of solid state materials determines their properties. The development of new, tuneable materials for technological demands requires flexible routes.

Basic requirements for compounds destined for materials science applications are purity, high yield synthetic routes, easy handling, facile storage and non-toxicity. Appropriate precursors should provide solubility or volatility which will determine the type of transformation, solution or in the vapour phase. Clean and low temperature decomposition pathways are desired for most applications. A stoichiometric matching of materials is then required if homogeneity is a goal. Materials are deposited from the gaseous state during CVD. Thus precursors for CVD processes must be volatile, but at the same time stable enough to make possible to be delivered to the reactor.

The deposition of electronic materials is an important and diverse area of contemporary research. Generally precursor compounds will only provide a single element to the deposited material, with others being volatilised during the CVD process. However, sometimes precursors may provide more than one. Such materials simplify the delivery system, as they reduce the number of reactants required to produce a given compound.

The 'precursor issues' are important for commercial and environmental reasons and include:

- The nature of the precursor: The most commonly used precursors were metal alkyls and/or main group hydrides, but such metal alkyls are often pyrophoric
and the hydrides are highly toxic. Such precursors therefore require special
equipment to guard against safety and environmental hazards.

- The tendency for homogeneous reaction in the MOCVD apparatus: this so
called pre-reaction causes snowing of the film that principally affects the
morphology of the growing layer.

- The need, in many cases, for large imbalance in the mole ratios of the
precursor materials. This is due to differences in volatility, thermal reactivity
of the precursors, and selective desorption from the growing layer.
Furthermore, the large excess of precursor exacerbates problems with waste.

Recently, it has been pointed out that the inorganic chemistry of the precursor (criteria
for precursor materials) is important in the control of:

- Impurities, especially dopants in the final material, which may originate from
the precursor.

- The phase of the final materials as determined by the decomposition
temperature of the precursor.

- Contamination of the material with the products of homogeneous reaction
within the reactor (homogeneous pre-reaction) of the precursors, e.g. ‘snow’
falling onto the substrate limiting morphology, this problem may in particular be
limited by using single molecule precursor.

- Vapour pressure. Suitable precursors are needed for deposition of materials
under low pressure conditions, LP-MOCVD. Many single molecule precursors
have rather low pressures and may need an MOMBE or LP-MOCVD approach.
For a compound to be considered as a suitable MOCVD precursor, certain properties should be adhered to. These include:

- The precursor should be relatively easy to synthesise, and prepared with a good degree of reproducibility.
- Highly volatile at moderate sublimation temperatures (low decomposition temperature).
- A sufficiently large temperature window between evaporation and decomposition.
- Clean decomposition without the incorporation of residual impurities (able to decompose cleanly to yield volatile and non-toxic by products).
- Compatibility with other precursors in the system.
- Easily synthesized in high yield, purity, cost and have long shelf life.

Various modifications have been made to conventional MOCVD methodologies in attempts to overcome such challenges. The use of precursor that has both the metal and the chalcogen in a single molecule can overcome some of the above problems. The conventional CVD process requires volatile precursors, which evaporate and provide steady, reproducible transport rates in the reactor. Another requirement is for a clean thermal decomposition pathway that leads to the deposition of good quality films at high rates and low temperatures.

Many MOCVD reactions involving hazardous toxic vapour phase precursors are undertaken at low pressure partly for reasons of safety; kinetic steps may also be enhanced at low pressure; solid precursors can be sublimed with or without a carrier gas. The vapour pressure of the precursor may be high enough not to require a carrier
gas, for example, \( \text{WF}_6 \) (VP 1000 Torr at 25 °C) can be used without a carrier gas to grow thin films; feed rate limitations usually do not occur.

Typical Precursor Materials: CVD precursor materials fall into a number of categories such as:

- Halides - \( \text{TiCl}_4, \text{TaCl}_5, \text{WF}_6 \).
- Hydrides - \( \text{SiH}_4, \text{GeH}_4, \text{AlH}_3(\text{NMe}_3)_2, \text{NH}_3 \).
- Metal organic Compounds.
- Metal alkyls - \( \text{AlMe}_3, \text{Ti(CH}_3\text{Bu})_4 \).
- Metal alkoxides - \( \text{Ti(O}^+\text{Pr})_4 \).
- Metal dialylamides - \( \text{Ti(NMe}_2)_4 \).
- Metal \( \beta \)-diketonates - \( \text{Cu(acac)}_2 \).

**Table 1.2:** Some typical precursors for MOCVD

<table>
<thead>
<tr>
<th>Type</th>
<th>Examples</th>
<th>Typical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal alkyls</td>
<td>( \text{Me}_2\text{Zn}, \text{Me}_3\text{Ga} )</td>
<td>Pyrophoric liquid or low MP solid</td>
</tr>
<tr>
<td>Metal hydrides</td>
<td>( \text{MH}_3\text{L} (M = \text{Ga or Al}) )</td>
<td>Useful in specialised applications</td>
</tr>
<tr>
<td>Hydrides</td>
<td>( \text{H}_2\text{S}, \text{PH}_3, \text{NH}_3 )</td>
<td>Permanent gases, highly toxic</td>
</tr>
<tr>
<td>Alternative group V or VI</td>
<td>( \text{BuSH}, \text{As(NR})_2_3 )</td>
<td>Reduced toxicity, lower temperatures and no pre-reaction</td>
</tr>
<tr>
<td>Coordination Complex</td>
<td>( [\text{M(acac)}_n (M = \text{Cu or Co}) )</td>
<td>Oxide deposition</td>
</tr>
<tr>
<td>Single source</td>
<td>( [\text{M(S}_2\text{CNR})_3] (R = alkyls) )</td>
<td>Metal sulphide and photovoltaic applications.</td>
</tr>
</tbody>
</table>
1.6 Applications of semiconductor thin films

1.6.1. Microelectronics
There is a continual drive for miniaturisation of electronic systems in the microelectronic industry, in addition to ensuring long-term reliability and low production costs. Applications in the field of electronics and microelectronics for which thin films play a significant role include the film capacitors, diodes (p-n junctions), transistors and photoconductors. The most common II-VI materials used as photoconductors are CdS, CdSe. Lead chalcogenide thin films have long been used for thin film infrared detectors. Copper indium diselenide is used in thin film form for photovoltaic solar energy conversion. Using this as the absorber layer and utilizing CdS along with ZnO as the window layer and hetero-junction partner, the solar conversion efficiency of the structure has attained more than 16%.\textsuperscript{13,66}

1.6.2. Optoelectronics
When the thermal equilibrium of a semiconductor is disturbed by the generation of electron and holes, recombination processes exist to restore the system to equilibrium. For direct band gap semiconductor, recombination can occur relatively with potentially high efficiency and forms the basis for a wide variety of photonic device applications. There are four basic groups that comprise photonic devices. Light emitting diodes (LEDs) and diode lasers (light amplification by stimulated emission of radiation) convert electrical energy to optical energy, whereas photo detectors and solar cells convert optical energy into an electrical output. Emission-based devices such as LEDs and injection lasers typically employ III-V compound semiconductors like GaAs as active elements.\textsuperscript{67-68}
1.6.3 Other applications

CVD has applications across a wide range of industries such as coatings. Coatings for a variety of applications such as wear resistance, corrosion resistance, high temperature protection, erosion protection and combinations thereof. Thin films of magnetic materials have found extensive use in coating for commercial materials such as data storage in computers.\(^{69}\)

Preforms can be infiltrated using CVD techniques to produce ceramic matrix composites such as carbon-carbon, carbon-silicon carbide and silicon carbide-silicon carbide composites. This process is sometimes called chemical vapour infiltration (CVI).

There has been an improvement in optical data storage capabilities on computer memory and compact disks. Organic polymer materials are deposited as a storage medium. CVD can be used to produce components that are difficult or uneconomical to produce using conventional fabrication techniques. Dense parts produced via CVD are generally thin-walled and may be deposited onto a mandrel. Thin films properties and applications are summarised in Table 1.3.
Table 1.3 Thin films applications

<table>
<thead>
<tr>
<th>Thin film property</th>
<th>Typical applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical</td>
<td>Reflective/antireflective coatings, interference filters, decoration (colour, lustre), memory discs, wave guides.</td>
</tr>
<tr>
<td>Electrical</td>
<td>Insulation, conduction, semiconductor devices, piezoelectric drivers</td>
</tr>
<tr>
<td>Magnetic</td>
<td>Memory disc</td>
</tr>
<tr>
<td>Chemical</td>
<td>Barriers to diffusion or alloying, protection against oxidation or corrosion, gas/liquid sensors</td>
</tr>
<tr>
<td>Mechanical</td>
<td>Hardness, adhesion, micromechanics</td>
</tr>
<tr>
<td>Thermal</td>
<td>Barrier layers, heat sinks</td>
</tr>
</tbody>
</table>
Chapter 2

Deposition of Platinum, Palladium and Nickel Chalcogenide Thin Films
2.1 General Introduction

The deposition of metal sulfide thin films has attracted considerable attention due to their use in many applications as discussed in chapter one. The platinum group metal chalcogenides are very useful in the electronics industry and they also have wide applications as catalysts in various industrial processes. Nakamoto and Kuriacose have reported the synthesis of thiocarbamato complexes of platinum and palladium from the reaction of an aqueous solution of ammonium dithiocarbamate with platinum or palladium salts. These complexes have been used as precursors for the preparation of the metal sulphide thin films. Revaprasadu, et al. deposited PtS and PdS thin films from bis(n-hexyl(methyl)dithiocarbamato)platinum(II) and bis(n-hexyl(methyl)dithiocarbamato)palladium(II), respectively.

There have been many reports on the synthesis and coordination chemistry of dichalcogenoimidodiphosphinate ligands of the type $R_2P(E)NHP(E)R_2$, were $E = O, S, Se$, and the $R = Et, iPr$, or "Bu. The coordination chemistry of these ligands are interesting as a consequence of the steric control that this ligand system may impart compared to, for example, acetylacetone (acac). They are readily prepared and offer an opportunity to vary both the donor atom and R group more easily than in the case of acetylacetone. Mixed donor imidodiphosphates can be easily prepared and show interesting structural differences using this ligand. Contrary to the complexes formed with acac, the ones with imidodiphosphinates show a variety of conformations of the six membered ring $MEPNPE'$, where $M =$ metal, and $E, E' =$ chalcogenide.
Deposition of Platinum, Palladium and Nickel Chalcogenide Thin Films

Metal complexes of imidodiphosphinato ligands are of particular interest due to the flexibility of the E-P-N-P-E back bone and their large E...E "bite", allowing the formation of chelate rings and resulting in a symmetrical coordination pattern through the donor atoms. Transition metal complexes incorporating Woollins ligands \{(iminobis(phosphinechalcogenide)} have demonstrated improved thermal and chemical stability over organic-based ligands such as β-diketone complexes, which are susceptible to oxidation, polymerisation and hydration. These metal complexes are excellent as single source precursors for chemical vapour deposition. The possibility of the selective coordination of metallic centres with imidodiphosphinate ligands through the manipulation of the R groups and the donor atoms E and E' play important roles in the deposition process. Dithiophosphinato complexes have found applications as solvent extraction reagents for metals, insecticides and pesticides, flotation agents for mineral ores, and additives to lubricant oils and can be used as a precursor for use in MOCVD. Metal complexes of the type \[M\{N(EPR_{x})_2\}_2\], where M = Ni, Pt, Pd, Sb, Zn, Hg, In, Ga, Pb, Cd, Co; R = Et, \textsuperscript{t}Pr, Ph, \textsuperscript{t}Bu; and E = S, Se or O have been prepared.\textsuperscript{94-105}

2.2 Experimental

2.2.1 Reagents

The following chemicals were used during this study without further purification: potassium tetrachloroplatinate(II) (95 %, Aldrich), potassium tetrachloropalladate (II) (95 %, Aldrich), nickel(II) chloride hexahydrate (Aldrich), chlorodiisopropyl alcohol (96%,Aldrich),chlorodiphenylphosphine(96%,Aldrich),1,1,3,3,3-hexamethyldisilazane (99.9 %, Aldrich), selenium powder (99.5+ %, Aldrich), sulfur
Deposition of Platinum, Palladium and Nickel Chalcogenide Thin Films

powder (Aldrich), petroleum ether (BDH), methanol (99 %, BDH), ethanol (BDH),
tetrahydrofuran (99 %, BDH), sodium methoxide (95 %, Aldrich), carbon disulfide
(Aldrich).

2.2.2 Synthesis of ligands

2.2.2.1 Synthesis of NH(SePPr2)2

The synthetic method is based on a literature procedure for preparing related
compounds.79 The reaction was performed under nitrogen using standard Schlenk line
techniques. A solution of P2PCI (4.87 g, 5.0 mL, 32 mmol) in toluene (100 mL) was
added drop wise to a solution of NH(SiMe3)2 (2.58 g, 3.4 mL, 16 mmol) in hot (50-60
°C) toluene (50 mL) over 30 min. Heating and stirring was continued for 3 h after
which time the reaction was cooled to room temperature and the selenium powder
was added (2.53 g, 31 mmol). The reaction was then refluxed for a further 6 h and
cooled to 0 °C. The resulting white precipitate was filtered off. Excess selenium was
removed by dissolving the product in CH2Cl2 and filtering through celite, followed by
the removal of solvent in vacuo. The crude product was recrystallized from CH2Cl2
and hexane (2:3 ratio) to give 4.25 g, 10.47 mmol, and 65 % yield of pure compound.
Mp: 170 °C. Anal. Calcd for C12H29NP2Se2: C, 35.38; H, 7.13; N, 3.44. Found: C,
35.49; H, 7.45; N, 3.42. FT-IR (KBr disc): v(N-H) 3211(s); δ (N-H) 1385(m); v
(PNP) 878(s); v(PSe) 489 cm⁻¹. ¹H NMR (CDCl3): 1.3 ppm ( 24 H, CH3); 2.3 (4 H,
CH); 7.1 (1H, NH). MS: m/z = 408 corresponds to [M + H]⁺.
2.2.2.2 Synthesis of NH(SP^iPr_2)_2

A solution of NH(P^iPr_2)_2 was prepared as described under section 2.2.2.1. Heating and stirring were continued for 3 h after which time the reaction was cooled to room temperature and sulfur powder added (1.0 g, 31 mmol). The reaction was then refluxed for further 6 h and cooled to 0 °C. The resulting white precipitate was filtered off and washed with CS_2 (2 x 10 mL) and light petroleum ether (2 x 10 mL). The crude product was recrystallised from CH_2Cl_2/hexane in 3:2 ratio. Yield: 0.17 g, 34 %. Mp: 165 °C. Anal. Calcd for C_{12}H_{19}NP_1S_1: C, 46.01; H, 9.27; N, 4.47; S, 20.45. Found: C, 45.79; H, 9.65; N, 4.54; S, 19.82. FT-IR (KBr disc): ν(N-H) 3243(s); ν(N-H) 1386(m); ν(pNP) 879(s); ν(pSe) 476 cm^{-1}. ^1H NMR (CDCl_3): 1.2 ppm (24 H, CH_3); 2.4 (4 H, CH); 7.2 (1 H, NH). MS: m/z = 314 corresponding to [NH(SP^iPr_2)_2]^+ with the expected isotopic distribution patterns.

2.2.2.3 Synthesis of NH(SePPh_2)_2

The compound NH(PPh_2)_2 (7.70 g, 20 mmol) and grey selenium (3.16 g, 40 mmol) were heated to reflux in sodium-dried toluene (150 mL) under nitrogen for 4 h. After cooling the solution the white precipitate was filtered off, washed with toluene (3 x 15 mL) and diethyl ether (3 x 15 mL) and dried in vacuo. Yield: 9.1 g, 84 %. Mp: 210 °C. Anal. Calcd for C_{24}H_{21}NP_2Se_2: C, 53.06; H, 3.90; N, 2.60. Found: C, 52.53; H, 3.80; N, 2.49. FT-IR (KBr disc): ν(PNP) 922(s); ν(PSe) 593(m), 545(m) cm^{-1}. MS: m/z = 544 corresponds to [NH(SePPh_2)_2]^+.
2.2.2.4 Synthesis of NH(SPPh₂)₂

A solution of (Ph₂)₂P(Cl, 4.87 g, 5.1 mL, 27 mmol) in toluene (100 mL) was added drop wise to a solution of NH(SiMe₃)₂, (2.58 g, 3.4 mL, 13.5 mmol) in hot (50-60 °C) toluene (50 mL) over 30 min. Heating and stirring were continued for 3 h after which time the reaction mixture was cooled to room temperature and the selenium powder was added (2.53 g, 31 mmol). The reaction was then refluxed for further 6 h and cooled to 0 °C. A white precipitate was obtained which was then filtered off, washed with toluene (3 x 15 mL) and diethyl ether (3 x 15 mL) and dried in vacuo. Yield: 5.2 g, 86 %. Mp: 218-220 °C. Anal. Calcd for C₂₇N₂P₂SZ: C, 64.13; H, 4.71; N, 3.12. Found: C, 62.89; H, 4.87; N, 3.48. FT-IR (KBr disc): v(pNP) 919(vs); v(PS) 649(s), 626(w) cm⁻¹. MS: m/z = 448 corresponds to [NH(SPPh₂)]⁺.

2.2.3 Synthesis of precursors

2.2.3.1 Synthesis of [Pt{N(SeI'Pr₂hhl]

An aqueous solution of K₂PtCl₄ (0.10 g, 0.25 mmol, 10 mL) was added to a yellow solution of NH(SeIPPr₂)₂ (0.2 g, 0.49 mmol) and CH₃ONa (0.027 g, 0.49 mmol) in methanol (30 mL). A yellow precipitate began to form after five minutes. The mixture was stirred for a further 30 min and the product, a yellow solid, was collected by filtration. The crude product was recrystallized from dichloromethane to give 0.09 g, (40 % yield) of the product. Mp: 138 °C. Anal. Calcd for C₂₄H₅₆N₂P₄PtSe₄: C, 28.61; H, 5.60; N, 2.78; P, 12.30. Found: C, 31.24; H, 6.38; N, 2.98; P, 12.33. FT-IR (KBr disc): v(PNP) 1181(s); v(PSe) 476(m); (NPSe) 412 cm⁻¹. ¹H NMR (CDCl₃): 1.2 ppm (48 H, CH₃); 7.2 ppm (1H, NH). MS: m/z = 1008 corresponding to [Pt{N(Pr₂PSe₂)₂}]⁺.
2.2.3.2 Synthesis of [Pt{N(SpPr$_2$)$_2$}] 

CH$_3$ONa (0.01 g, 0.16 mmol) and NH(SpPr$_2$)$_2$ (0.05 g, 0.16 mmol) in methanol (30 mL) was added to an aqueous solution of K$_2$PtCl$_4$ (0.03 g, 0.08 mmol, 10 mL). The solution was refluxed for 2 h giving a yellow solution. The solvent was removed in vacuo and the yellow solid crude product was recrystallised from acetone.

Yield: 0.032 g, 49 %. Mp: 169 °C. Anal. Calcd for C$_{24}$H$_{56}$N$_2$P$_4$PtS$_4$: C, 36.16; H, 6.88; N, 3.42. Found: C, 37.60; H, 7.15; N, 3.39. FT-IR (KBr disc): $\nu$ (PNP) 1222(s); $\nu$ (PS) 628(m); $\nu$ (NPS) 413 cm$^{-1}$. $^1$H NMR (CDCl$_3$): 1.2 ppm (48 H, CH$_3$); 2.3 ppm (8H, CH); 7.2 ppm (1H, NH). MS: m/z = 819 corresponding to [Pt{N(SpPr$_2$)$_2$}]$_2$.

2.2.3.3 Synthesis of [Pd{N(SePr$_2$)$_2$}] 

An aqueous solution of K$_2$PdCl$_4$ (0.08 g, 0.25 mmol, 10 mL) was added to a yellow solution of NH(SePr$_2$)$_2$ (0.2 g, 0.49 mmol) and CH$_3$ONa (0.0266 g, 0.492 mmol) in methanol (30 mL). The resulting blood red solution was stirred and then the solvent was removed in vacuo to give red solid product. The product was extracted from dichloromethane yielding 0.12 g, 0.13 mmol, 58 % of pure compound. Mp: 186 °C.

Anal. Calcd for C$_{24}$H$_{56}$N$_2$P$_4$PdSe$_4$: C, 31.37; H, 6.14; N, 3.05; P, 13.48. Found: C, 31.50; H, 6.34; N, 2.98; P, 13.55. FT-IR (KBr disc): $\nu$ (PNP) 1182(s); $\nu$ (PSe) 476(m); $\nu$ (NPS) 412 cm$^{-1}$. $^1$H NMR (CDCl$_3$): 1.3 ppm (48 H, CH$_3$); 2.3 ppm (8H, CH); 7.2 ppm (1H, NH). MS: m/z = 918 corresponds to [Pd{N(Pr$_2$PSe)$_2$}]$_2$.

36
2.2.3.4 Synthesis of \([\text{Pd}\{\text{N}(\text{SP}^3\text{Pr}_2)\}_2]\)

Deprotonation of \(\text{NH}(\text{SP}^3\text{Pr}_2)_2\) (0.05 g, 0.16 mmol) with \(\text{CH}_3\text{ONa}\) (0.00865 g, 0.16 mmol) in methanol (30 mL) to give \(\text{Na}[\text{N}(\text{Pr}_2\text{PS})_2]\) was followed by addition of an aqueous solution of \(\text{K}_2\text{PtCl}_4\) (0.03 g, 0.08 mmol, 10 mL). The solution turned from yellow to red/orange immediately. The mixture was stirred for further 30 min and the solvent was removed \textit{in vacuo} and the solid product was recrystallised from acetone. Yield: 0.035 g, 59 %. Mp: 164 °C. Anal. Caled for \(\text{C}_2\text{H}_5\text{N}_2\text{P,J,dS}_4\): C, 39.42; H, 7.72; N, 3.83. Found: C, 39.71; H, 7.74; N, 3.73. FT-IR (KBr disc): \(\nu(\text{PNP})\) 1200 (s); \(\nu(\text{PS})\) 543 (m); \(\nu(\text{NPS})\) 420 cm\(^{-1}\). \(^1\text{H}\) NMR (CDCl\(_3\)): 1.3 ppm (48 H, CH\(_3\)); 2.3 ppm (8H, CH); 7.2 ppm (1H, NH). MS: m/z = 731 corresponds to \([\text{Pd}\{\text{N}(\text{SP}^3\text{Pr}_2)\}_2]\).

2.2.3.5 Synthesis of \([\text{Pd}\{\text{N(SePPh}_2)_2\}_2]\)

An aqueous solution of \(\text{K}_2\text{PdCl}_4\) (0.03 g, 0.092 mmol, 10 mL) was added to a yellow solution of \(\text{NH}(\text{SePPh}_2)_2\) (0.1 g, 0.18 mmol) and \(\text{CH}_3\text{ONa}\) (0.01 g, 0.16 mmol) in acetone (10 mL). The solution turned red immediately and then turned orange. The reaction mixture was stirred 1 h at room temperature and the solvent was removed \textit{in vacuo}. The solid crude product was recrystallised from CH\(_2\)Cl\(_2\) and dried under vacuum. The red filtrate was allowed to evaporate to give a pure red product. Yield: 0.09 g, 83 %. Mp: 270 °C. Anal. Caled for \(\text{C}_{48}\text{H}_{40}\text{N}_2\text{P}_4\text{PdSe}_4\): C, 48.40; H, 3.39; N, 2.35. Found: C, 48.60; H, 3.15; N, 2.29. FT-IR (KBr disc): \(\nu(\text{PNP})\) 1153 (m), 804; \(\nu(\text{PSe})\) 537 (vs) cm\(^{-1}\). MS: m/z = 544 correspond to \([\text{NH}(\text{SePPh}_2)_2]^+\) and 1192 corresponds to \([\text{Pd}\{\text{N(SePPh}_2)_2\}_2]^+\).
2.2.3.6 Synthesis of \([\text{Pt}\{\text{N(SePPh}_2\}_2\}_2]\)

An aqueous solution of \(\text{K}_2\text{PtCl}_4\) (0.04 g, 0.09 mmol, 10 mL) was added to a yellowish solution of \(\text{NH}\{\text{SePPh}_2\}_2\) (0.1 g, 0.18 mmol) and \(\text{CH}_3\text{ONa}\) (0.01 g, 0.18 mmol) in acetone (10 mL) under nitrogen to give an intense yellow solution. A yellow precipitate begins to be formed. The mixture was stirred for 1 h. The precipitate was filtered off and then recrystallised from acetone. Yield: 0.1 g; 87 %. Mp: 210 ºC. Anal. Calcd for \(\text{C}_{48}\text{H}_{w}\text{N}_2\text{P}_6\text{Se}_4\): C, 45.05; H, 3.15; N, 2.19. Found: C, 46.86; H, 2.77; N, 2.12. FT-IR (KBr disc): \(v\) (PNP) 1174(s), 803(s); \(v\) (PSe) 545 (vs) cm\(^{-1}\). MS: \(m/z = 544\) corresponds to \([\text{NH}\{\text{SePPh}_2\}_2]^{+}\) and 1280 corresponds to \([\text{Pt}\{\text{N(SePPh}_2\}_2\}_2]^{+}\).

2.2.3.7 Synthesis of \([\text{Pd}\{\text{N(SPPPh}_2\}_2\}_2]\)

An aqueous solution of \(\text{K}_2\text{PdCl}_4\) (0.036 g, 0.111 mmol, 10 mL) was added to a solution of \(\text{NH}\{\text{SPPPh}_2\}_2\) (0.1 g, 0.22 mmol) and \(\text{CH}_3\text{ONa}\) (0.012 g, 0.22 mmol) in acetone (10 mL). The solution turns orange immediately and the reaction mixture was stirred for 1 h. The solvent was removed \textit{in vacuo} and the solid crude product was recrystallised from \(\text{CH}_2\text{Cl}_2\). The orange filtrate was evaporated by vacuum line to give a pure product. Yield: 0.1 g, 90 %. Mp: 310 ºC. Anal. Calcd for \(\text{C}_{48}\text{H}_{w}\text{N}_2\text{P}_6\text{S}_4\): C, 57.45; H, 4.02; N, 2.79. Found: C, 57.80; H, 3.66; N, 2.67. FT-IR (KBr disc): \(v\) (PNP) 1157(m), 805(s); \(v\) (PS) 536(m) cm\(^{-1}\). MS: \(m/z = \) Molecular ions peaks \([\text{Pd}\{\text{N(SPPPh}_2\}_2\}_2]^{+}\) at 1002 and \([\text{N(SPPPh}_2\}_2]^{+}\) at 448 revealed the expected, characteristic, isotopic distribution patterns.
2.2.3.8 Synthesis of [Pt{N(SPPh₂)₂}]₂

An aqueous solution of K₂PtCl₄ (0.038 g, 0.09 mmol, 10 mL) was added to a solution of NH(SPPh₂)₂ (0.1 g, 0.18 mmol) and CH₃ONa (0.01 g, 0.18 mmol) in acetone (10 mL). The solution was stirred for 14 h under nitrogen to give an intense yellow solution. The product was filtered, washed with distilled water (10 mL) and methanol (10 mL). Yield: 0.08 g, 67 %. Mp: 205 °C. Anal. Calcd for C₄₈H₄₀N₂P₄PtS₄: C, 52.79; H, 3.69; N, 2.57. Found: C, 56.05; H, 3.77; N, 2.68. FT-IR (KBr disc): ν (pNP) 1109 (m); ν (PS) 562 (m) cm⁻¹. MS: m/z = Molecular ions peaks [Pt{N(SPPh₂)₂}]²⁺ at 1091 and [N(SPPh₂)]²⁺ at 448 revealed the expected, characteristic, isotopic distribution patterns.

2.2.3.9 Synthesis of [Ni{N(SePPr₂)₂}]₂

An aqueous solution of NiCl₂.6H₂O (0.0292 g, 0.122 mmol, 10 mL) was added to a yellow solution of NH(SePPr₂)₂ (0.1 g, 0.245 mmol) and CH₃ONa (0.0133 g, 0.245 mmol) in methanol (20 mL). A brown precipitate began to form after five minutes. The mixture was stirred at room temperature for a further 30 min and the product, a brown solid, was collected by filtration. The crude product was washed three times with methanol (3 x 10 mL). Yield: 0.091 g, 83 %. Mp: 138 °C. Anal. Calcd for C₂₄H₅₆N₂P₄NiSe₄: C, 33.09; H, 6.48; N, 3.22. Found: C, 29.06; H, 5.68; N, 2.79. FT-IR (KBr disc): ν (PNP) 1178 (s); ν (PSe) 480 (m); (NPSe) 416 cm⁻¹. MS: m/z = 871 corresponds to [Ni{N(SePPr₂)₂}] and 407 corresponds to NH(SePPr₂)₂.
2.2.3.10 Synthesis of [Ni{N(SPiPr2hhl}\[2]

An aqueous solution of NiCl2.6H2O (0.1 g, 0.319 mmol, 10 mL) was added to a yellow solution of NH(Spiprzh (0.0379 g, 0.159 mmol) and CH3ONa (0.018 g, 0.319 mmol) in methanol (20 mL). A green precipitate began to form after five minutes. The mixture was stirred at room temperature for a further 30 min and the product, a green solid, was collected by vacuum filtration. The crude product was washed three times with methanol (3 x 10 mL). Yield: 0.183 g, 84 %. MP = 125 °C. Anal. Calcd for C24H56N2P~iS4: C, 42.17; H, 8.26; N, 4.60. Found: C, 42.03; H, 8.29; N, 4.03. FT-IR (KBr disc): v (pNP) 1208(s); v (pSe) 646(m); (NPS) 425 cm⁻¹. MS: m/z = 683 corresponds to [Ni{N(SPiPr2}2]₂.

2.2.3.11 Synthesis of [Ni{N(SPPh 2)2}2]

A methanolic solution of NiCl2.6H2O (0.265 g, 0.111 mmol, 10 mL) was added to a solution of NH(SPPh 2)2 (0.1 g, 0.222 mmol) and CH3ONa (0.0120 g, 0.111 mmol) in methanol (10 mL). The solution was stirred at room temperature overnight. The product was filtered, washed three times with methanol (3 x 10 mL). Yield: 0.071 g, 67 %. Anal. Calcd for C48H4N2P4NiS4: C, 60.32; H, 4.22; N, 2.93. Found: C, 60.44; H, 4.27; N, 2.88. FT-IR (KBr disc): v (PNP) 1152(s); v (PS) 808(m); 540(m) cm⁻¹. MS: m/z = 449 corresponds to [Ni{N(SPPh2}2]⁺ ligands.

2.2.3.12 Synthesis of [Ni{N(SePPh2)2}2]

A methanolic solution of NiCl2.6H2O (0.0876 g, 0.368 mmol, 10 mL) was added to a solution of NH(SePPh2)2 (0.4 g, 0.736 mmol) and CH3ONa (0.0397 g, 0.73 mmol) in acetone (10 mL). The solution was stirred at room temperature for 14 h under
nitrogen. The product was filtered, washed with distilled water (10 mL) followed by three times with methanol (3 x 10 mL). Yield: 0.351 g, 83 %. Anal. Calcd. for C_{48}H_{40}N_{2}P_{4}NiSe_{4}: C, 50.43; H, 3.53; N, 2.45. Found: C, 50.47; H, 3.55; N, 2.42. FT-IR (KBr disc): v(PNP) 1190 (s); v(PS) 806(m); 527(vs) cm\(^{-1}\).

2.3 Thin film deposition by CVD

2.3.1 Deposition techniques

A standard method was adopted for the cleaning of the substrates prior to the CVD process in order to achieve reproducible results. The following procedure was used to clean conventional microscopic slides:

- Substrate (glass) were immersed in 50 % nitric acid overnight.
- This was followed by rinsing the substrates in deionised water.
- The substrates were then placed in the micro-oven for drying at 150 °C for 1 h.

_Growth of thin films by AACVD:_ The precursor was dissolved in toluene with the average amount utilised being 0.2 g in 30 mL of toluene. The solution was placed in a two necked 100 mL flask with a gas inlet that allowed nitrogen to pass into the solution (to aid transport of aerosol). The tube held a number of glass substrate that were distributed along the length of these and they were heated in a carbolite furnace to the temperature prior to deposition. An aerosol was then generated by the piezoelectric modulator of an ultrasonic humidifier and nitrogen gas passed through the aerosol mist, directing the aerosol to the CVD reactor. A Platon flow gauge was used to control the flow rate of 200 sccm, enabling controlled delivery of aerosol droplets into the deposition chamber. The aerosol was then allowed to flow over the substrate for a specified time.
Preparation of thin films by LP-MOCVD: Film deposition experiments were conducted in a cold-wall and low pressure MOCVD reactor, equipped with a graphite susceptor heated by a 1 kW tungsten-halogen lamp and with a water-cooled reflector. For each run, the reactor was loaded with a ca. 200 mg of the precursor and then evacuated (0.05 Torr) with a rotary evaporator, via a liquid nitrogen trap. A Carbolite tube furnace was used to transport the precursor (0.2 g) under vacuum. The substrate was placed on the susceptor, the temperature of the susceptor varied between 200-600 °C and the running time varied between 1 h and 2 h. To start a deposition run the loaded reactor was inserted into a tube furnace set at 150 °C. The substrate used in film deposition was glass.

2.3.2 Instrumentation and physical measurements

2.3.2.1 Elemental analysis
Elemental analysis was conducted at the Microanalytical laboratories at the University of Manchester, UK.

2.3.2.2 Thermogravimetric analysis (TGA)
TGA measurements were carried on a Seiko SSC/S200 model under nitrogen atmosphere (flow rate 20 mL/min), from 25 to 500 °C, with a heating rate of 10 °C/min.

2.3.2.3 Infrared spectra
Infrared spectra were recorded using a Perkin Elmer Paragon 1000 FT-IR (4000-400 cm⁻¹, resolution ± 4 cm⁻¹). Samples were prepared as KBr pellets.
2.3.2.4 NMR spectroscopy

NMR studies ($^1$H and $^{13}$C) were carried out using a Bruker AC300 FTNMR spectrometer, using CDCl$_3$ or DMSO as solvents.

2.3.2.5 Mass Spectroscopy

Mass spectra were recorded on a Kratos concept 1S instrument.

2.3.2.6 X-ray diffraction (XRD)

X-ray diffraction studies were performed using secondary graphite monochromated Cu Kα radiation (40 kV) on either a Philips X’Pert Materials Diffractometer (APD) or Bruker AXS D8 diffractometer. Measurements were taken using a glancing angle incidence detector at an angle of 3°, for 2θ values over 10-95° in steps of 0.04° with a count time of 2 s. The scans were done over 2θ values of 5-90° and a step size of 0.01° or 0.02°.

2.3.2.7 Scanning electron microscopy (SEM)

Films were carbon coated using Edward’s E306A coating system before SEM analysis. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX) for films deposited in the earlier part of this study were carried out on a Phillips 525 SEM instrument with an EDAX 9100 EDS unit. Prior to characterisation, samples were either carbon coated (using an Edwards coating system E 306A) to allow EDAX analysis or otherwise gold coated (Edwards sputter coater S150B).
2.4 Results and discussions

The $^1$H NMR spectra, mass spectra, and microanalysis were satisfactory for all compounds. The synthesis of ligands NH(EPR$_2$)$_2$, (where E = S, Se, and the R = $^i$Pr, Ph$_2$) were carried out according to previously reported methods. The synthesis of the precursors involves the deprotonation of the N-H moiety, using sodium methoxide to form anionic species which subsequently reacted with the metal salt to form the complexes. The compounds prepared were found to be ideal for use as single source precursors; they are air stable and readily obtained in good synthetic yields.

2.4.1 Infrared

The solid-state (KBr pellets) IR spectra of the complexes were also examined and the bands for the $\nu$(P-S) or $\nu$(P-Se) and $\nu$(P-N-P) stretching vibrations were assigned. The $\nu$(NH) band is observed around 3000 cm$^{-1}$ for all compounds. Characteristic $\nu$(PNP) bands were also observed at 800-930 cm$^{-1}$. Characteristic bands were observed, indicating the change in bond order that occurred upon removal of the amine proton, in particular the marked increase in the frequency of the $\nu$(PNP) vibration to 1100-1200 as the negative charge is delocalised over the ligand. As observed in related systems there is an increase in the frequency of $\nu$(PNP) vibration in the complexes compared with the free ligand.
Table 2.1 Infrared spectra (cm\textsuperscript{-1}) of the ligands

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<tr>
<th></th>
<th>([\text{NH(EP}^\text{Pr}_2\text{)}_2])</th>
<th>([\text{NH(EP}^\text{Ph}_2\text{)}_2])</th>
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<td>3243 (s)</td>
<td>3211(s)</td>
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<td>1386 (m)</td>
<td>1385(m)</td>
</tr>
<tr>
<td>(\nu(\text{PNP}))</td>
<td>879 (s)</td>
<td>878(s)</td>
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<tr>
<td>(\nu(\text{P-E}))</td>
<td>476 (s)</td>
<td>489 (m)</td>
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Table 2.2 Infrared spectra (cm\textsuperscript{-1}) for the precursors

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<th>Compound formula</th>
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<th>(\nu(\text{PE}))</th>
<th>(\nu(\text{NPE}))</th>
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<td>1. ([\text{Pt}{\text{N(SeP}^\text{Pr}_2\text{)}_2}_2])</td>
<td>1181(s)</td>
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<td>2. ([\text{Pt}{\text{N(SeP}^\text{Ph}_2\text{)}_2}_2])</td>
<td>1222(s)</td>
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<td>3. ([\text{Pd}{\text{N(SeP}^\text{Pr}_2\text{)}_2}_2])</td>
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<td>4. ([\text{Pd}{\text{N(SeP}^\text{Ph}_2\text{)}_2}_2])</td>
<td>1200(s)</td>
<td>543(m)</td>
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<td>5. ([\text{Pt}{\text{N(SePP}^\text{Ph}_2\text{)}_2}_2])</td>
<td>1174(s)</td>
<td>803(s)</td>
<td>545(vs)</td>
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<td>6. ([\text{Pt}{\text{N(SPP}^\text{Ph}_2\text{)}_2}_2])</td>
<td>1109(m)</td>
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<td>540</td>
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<tr>
<td>7. ([\text{Pd}{\text{N(SePP}^\text{Ph}_2\text{)}_2}_2])</td>
<td>1153(m)</td>
<td>804(m)</td>
<td>537(vs)</td>
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<tr>
<td>8. ([\text{Pd}{\text{N(SPP}^\text{Ph}_2\text{)}_2}_2])</td>
<td>1157(m)</td>
<td>805(s)</td>
<td>536(m)</td>
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<tr>
<td>9. ([\text{Ni}{\text{N(SeP}^\text{Pr}_2\text{)}_2}_2])</td>
<td>1178(s)</td>
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<td>416(m)</td>
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<td>10. ([\text{Ni}{\text{N(SeP}^\text{Ph}_2\text{)}_2}_2])</td>
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<td>425(m)</td>
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<tr>
<td>12. ([\text{Ni}{\text{SPP}^\text{Ph}_2\text{)}_2}_2])</td>
<td>1152(s)</td>
<td>808(m)</td>
<td>540(m)</td>
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</table>

\(E = \text{S or Se}\)
There is closeness in results for the \( u(P-S) \) vibration in all complexes. Furthermore, it has been observed\(^9\), in related systems, that there is a marked increase in the frequency of the \( u(PNP) \) vibration of the compound compared to the free ligand. The deprotonation of the ligand on complexation leads to the loss of the \((N-H)\) band in the IR spectra.

### 2.4.2 Single crystal X-ray structure analysis of \([Pt\{N(Se^1Pr_2)\}_2]\)\([2]\)

Crystals suitable for X-ray diffraction studies were obtained by slow diffusion of hexane into dichloro-methane solutions of the precursor. Data were collected at 100(2) K using graphite–monochromated Mo K\(\alpha\) radiation (\( \lambda = 0.71073 \) Å) by the Bruker APEX diffractometer. Details of data collection and structure refinements are presented in Table 2.3.

All X-ray measurements were made at room temperature using suitable crystals for data collection. All calculations were carried out using SHELXTL package. All non-hydrogen atoms were refined with isotropic atomic displacement parameters. Hydrogen atoms were placed in calculated positions, assigned anisotropic thermal parameters and allowed to ride on their parent carbon atoms. The structure is isomorphous with the selenium analogue. Accurate lattice parameters were determined from least squares refinement of well centered reflection in the range \( 2.03 \leq \theta \leq 28.27 \). During data collection three standard reflections were periodically observed and show no significant intensity variations. The range of \( h, k, \) and \( l \) are \(-6 \leq h \leq 13, -19 \leq k \leq 19, -15 \leq l \leq 13 \). Total numbers of measured and observed independent reflection are 10821 and 4077 (\( R_{int} = 0.0410 \)). The final R and \( R_w \) values are given in the Table 2.3. The ORTEP representation of the complex is illustrated in Figure 2.1.
The selected intra and intermolecular bond lengths and angles for the complex are summarised in Table 2.4. The crystal system is monoclinic with the space group of P2(1)/C.

The X-ray crystal structure has been previously reported but the method used here is different from the literature. The PtSe₂P₂N ring of the previously reported structure adopts a pseudo-chair confirmation whereas the recent structure reveals square-planar structure where the six membered PtSe₂P₂N ring adopts a distorted "boat" conformation. The crystal structure cores are similar to those reported in the literature. The platinum complex structure reveals that the complex consists of square-planar metal centre with two chelating ligands. When compared with the free ligand, the P—S bond is lengthened and the P—N bonds are shortened, consistent with some electron delocalisation around the rings. This suggests that some π-delocalisation occurs upon deprotonation and chelate formation. The six membered rings PtSe₂P₂N of the recent structure adopt a linear pseudo chair conformation. The conformational differences of the PtSe₂P₂N rings do not appear to have dramatic effects on the bond lengths, although there are a number of noticeable angular changes. Thus, whilst Se(1)-Pt-Se(2) is 90°, the equivalent angle is enlarged to 101° in the reported literature. The Se atoms are arranged in a linear tetrahedron with the Se—Pt—Se angles varying from 180 and 90°. The P(1)-N(1)-P(2) angle is also significantly reduced than the reported literature, from 138° to 127°. The packing diagram shows a sandwich structure, which further confirms 1(metal):2 (ligand) ratios (Figure 2.2).
Figure 2.1 Single X-ray structure of $[\text{Pt}\{\text{N(Se}^{\text{Pr}}_{2})_{2}\}]$
Figure 2.2 Packing diagram of [Pt\(N(SePr_2)_2\)]_2\]
Table 2.3 Crystal data and structural refinement details for [Pt{N(SePr$_2$)$_2$}]$_2$

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<td>Crystal System, space group</td>
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<td>b = 8.765(3) Å</td>
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<td>c = 11.8990(12) Å</td>
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<td>Z, Calculated density</td>
<td>2, 1.926 mg/m$^3$</td>
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<tr>
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<tr>
<td>F(000)</td>
<td>976</td>
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<tr>
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<tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>Completeness to theta = 26.41</td>
<td>94.7%</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.6780 and 0.2835</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>4077/18/168</td>
</tr>
<tr>
<td>Goodness-of-fit on F$^2$</td>
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<td>Final R indices [I &gt; 2 sigma (I)]</td>
<td>R1 = 0.0640, wR2 = 0.1819</td>
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<td>R indices (all data)</td>
<td>R1 = 0.0729, wR2 = 0.1870</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>3.535 and -5.751 e.A$^{-3}$</td>
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</table>
Table 2.4 Selected bond length (Å) and angles (deg) for [Pt\{N\{Se^1Pr_2\}_2\}_2]

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<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Angle (deg)</th>
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<tr>
<td>Pt(1) – Se(1)</td>
<td>2.5231(10)</td>
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</tr>
<tr>
<td>Pt(1) – Se(2)</td>
<td>2.5323(10)</td>
<td></td>
</tr>
<tr>
<td>P(1) – Se(1)</td>
<td>2.187(2)</td>
<td></td>
</tr>
<tr>
<td>P(2) – Se(2)</td>
<td>2.195(2)</td>
<td></td>
</tr>
<tr>
<td>N(1) – P(1)</td>
<td>1.592(8)</td>
<td></td>
</tr>
<tr>
<td>N(1) – P(2)</td>
<td>1.592(8)</td>
<td></td>
</tr>
<tr>
<td>Se(1) – Pt(1) – Se(1)</td>
<td>180.0</td>
<td></td>
</tr>
<tr>
<td>Se(1) – Pt(1) – Se(2)</td>
<td>90.06(3)</td>
<td></td>
</tr>
<tr>
<td>P(1) – Se(1) – Pt(1)</td>
<td>94.62(7)</td>
<td></td>
</tr>
<tr>
<td>P(2) – Se(2) – Pt(1)</td>
<td>100.04(7)</td>
<td></td>
</tr>
<tr>
<td>N(1) – P(1) – Se(1)</td>
<td>116.7(3)</td>
<td></td>
</tr>
<tr>
<td>N(1) – P(2) – Se(2)</td>
<td>119.2(3)</td>
<td></td>
</tr>
<tr>
<td>P(2) – N(1) – P(1)</td>
<td>138.0(5)</td>
<td></td>
</tr>
</tbody>
</table>

2.4.3 Single crystal X-ray structure analysis of [Pd\{N\{SPh_2\}_2\}_2]

Crystals suitable for X-ray diffraction studies were obtained by dissolving the complex in hot dimethyl sulfoxide (DMSO). Crystal were formed immediately on cooling and filtered to separate them from DMSO. Data were collected at 293(2) K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) on Bruker APEX diffractometer. Details of data collection and structure refinements are shown in Table 2.5.

This structure was solved by direct methods using SHELXL-93 [31] and refined by full-matrix least-squares on \( F^2 \). X-ray crystallography studies revealed that the complex is tetrahedrally coordinated by two ligands through sulfur atoms of the ligand, as shown in Figure 2.3. The compound consists of discrete, monomeric molecules in which the ligands are found to be bidentate, conferring distorted tetrahedral coordination geometry around the palladium centres. Selected inter atomic distances and angles are summarised in Table 2.6.
Non-hydrogen atoms were refined isotropically and hydrogens were included in fixed positions. However, the P—S bonds in the complex are significantly longer than those of the free ligand, while the P—N bonds are significantly shorter. This suggests that some p-delocalisation occurs upon deprotonation and chelate formation. Despite this, the conformation of the PdS$_2$P$_2$N rings in the compound (Figure 2.3) adopts a puckered, pseudo boat geometry, with sulfur and phosphorus atoms at the apices. The resulting PdS$_2$P$_2$N chromophores are found to be puckered. The bond lengths and angles are in good agreement with the previously reported literature even though the methods for preparation are different. The packing diagram of [Pd\{N(SPh)$_2$$_2$\}]$_2$ is shown in Figure 2.4.
Figure 2.3 Single X-ray structure of [Pd\{N(SPh)_{2}\}_{2}]

Deposition of Platinum, Palladium and Nickel Chalcogenide Thin Films
Figure 2.4 Packing diagram of [Pd{N(SPh$_2$)$_2$}]$_2$
### Table 2.5 Crystal data and structural refinement details for [Pd(N(SPh)2)2]2

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
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<tr>
<td><strong>Empirical formula</strong></td>
<td>C₄₈H₆₀N₂P₄PdS₄</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>1003.34</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>100(2) K</td>
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<tr>
<td><strong>Wavelength</strong></td>
<td>0.71073 Å</td>
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<tr>
<td><strong>Crystal System, space group</strong></td>
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</tr>
<tr>
<td><strong>Unit cell dimensions</strong></td>
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</tr>
<tr>
<td>a</td>
<td>25.031(10) Å</td>
</tr>
<tr>
<td>α</td>
<td>90°</td>
</tr>
<tr>
<td>b</td>
<td>8.765(3) Å</td>
</tr>
<tr>
<td>β</td>
<td>114.36(6)°</td>
</tr>
<tr>
<td>c</td>
<td>22.325(8) Å</td>
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<td>γ</td>
<td>90°</td>
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<tr>
<td><strong>Volume</strong></td>
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<td><strong>Z, Calculated density</strong></td>
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<tr>
<td><strong>Absorption coefficient</strong></td>
<td>0.784 mm⁻¹</td>
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<td><strong>F(000)</strong></td>
<td>2048</td>
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<tr>
<td><strong>Crystal size</strong></td>
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<tr>
<td><strong>Theta range for data collection</strong></td>
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</tr>
<tr>
<td><strong>Limiting indices</strong></td>
<td>-31&lt; = h &lt; = 31, -10&lt; = k &lt; = 10, -27&lt; = l &lt; = 27</td>
</tr>
<tr>
<td><strong>Reflections collected/unique</strong></td>
<td>16060/4556 [R(int) = 0.0287]</td>
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<tr>
<td><strong>Completeness to theta = 26.41</strong></td>
<td>99.4 %</td>
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<tr>
<td><strong>Absorption correction</strong></td>
<td>Semi-empirical from equivalents</td>
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<td><strong>Max. and min. transmission</strong></td>
<td>0.8915 and 0.7445</td>
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<td><strong>Refinement method</strong></td>
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<td><strong>Goodness-of-fit on F²</strong></td>
<td>1.021</td>
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<td><strong>Final R indices [I &gt; 2 sigma (I)]</strong></td>
<td>R1 = 0.0324, wR2 = 0.0771</td>
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<td><strong>R indices (all data)</strong></td>
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<td><strong>Largest diff. peak and hole</strong></td>
<td>0.637 and -0.490 e.A⁻³</td>
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Table 2.6 Selected bond length (Å) and angles (deg) for [Pd{N(SPh$_2$)$_2$}]$_2$

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Length/Angle</th>
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<td>Pd(1) − S(1)</td>
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<td>Pd(1) − S(2)</td>
<td>2.3278(9)</td>
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<tr>
<td>S(1) − P(1)</td>
<td>2.0241(11)</td>
</tr>
<tr>
<td>S(2) − P(2)</td>
<td>2.0265(12)</td>
</tr>
<tr>
<td>P(1) − N(1)</td>
<td>1.601(2)</td>
</tr>
<tr>
<td>P(2) − N(1)</td>
<td>1.596(2)</td>
</tr>
<tr>
<td>S(1) − Pd(1) − S(1)</td>
<td>180.0</td>
</tr>
<tr>
<td>S(2) − Pd(1) − S(1)</td>
<td>80.93(3)</td>
</tr>
<tr>
<td>P(1) − S(1) − Pd(1)</td>
<td>98.46(4)</td>
</tr>
<tr>
<td>P(2) − S(2) − Pd(1)</td>
<td>108.26(16)</td>
</tr>
</tbody>
</table>

2.4.4 The TGA analysis of [Pt{N(SeP$_3$Pr$_3$)$_2$}]$_2$

The thermogravimetric analysis (TGA) curve shown in Figure 2.5 reveals that the complex decomposed between ca. 213-348 °C with a weight loss of 87 % (Table 2.12). This is a one-step decomposition which makes the precursor suitable for both LP-MOCVD and AACVD deposition of thin films.

![Figure 2.5 TGA curve of [Pt{N(SeP$_3$Pr$_3$)$_2$}]$_2$](image)
2.4.5 Growth of PtSe₂ thin films from [Pt{N(SePPr₂)₂}₂]

Deposition experiments were carried out at various deposition temperatures between 400-475 °C, but the films were grown between 400 to 450 °C. The precursors were held in a tube furnace heated at temperatures in the range 400-475 °C. The precursor temperature was kept constant at 225 °C and the substrate temperatures were varied between 400-475 °C.

Good quality crystalline films were grown on the glass substrate at these temperatures region. The films obtained were brownish in colour, adherent to the glass substrate surface but could be removed by scratching the surface using a scalpel. No growth of thin films was observed below 400 °C and above 450 °C.

Figure 2.6 XRD pattern of PtSe₂ films deposited from [Pt{N(SePPr₂)₂}₂] at (a) 400, (b) 425, and (c) 450 °C with T_{prec} = 225 °C
Energy dispersive X-ray (EDAX) confirms the presence of platinum and selenide in ca. 1:2 ratios. X-ray diffraction patterns of the PtSe₂ (JCPDS 18-0970) thin films deposited on glass indicate that the films are highly crystalline.

At higher deposition temperatures, the degree of crystallinity of the as deposited films improved as indicated by the intensity of the XRD peaks, i.e. greater resolution (Figure 2.6).

The XRD patterns obtained from the films revealed only single phase (hexagonal) were deposited with a preferred orientation along the (001) plane (Figure 2.6).

The precursor was also used for the growth of platinum selenide thin film by AACVD to investigate any phase changes of PtSe₂ films. However, films were noncrystalline materials, which were confirmed by the XRD.

Table 2.7: XRD data of PtSe₂ thin films

<table>
<thead>
<tr>
<th>hkl</th>
<th>d(lit)/Å (%)</th>
<th>d(exp)/Å (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>001</td>
<td>5.08 (40)</td>
<td>5.13 (95)</td>
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<tr>
<td>101</td>
<td>2.72 (100)</td>
<td>1.42 (33)</td>
</tr>
<tr>
<td>102</td>
<td>1.99 (50)</td>
<td>1.07 (3)</td>
</tr>
<tr>
<td>200</td>
<td>1.61 (5)</td>
<td>1.84 (3)</td>
</tr>
<tr>
<td>003</td>
<td>1.69 (5)</td>
<td>0.94 (3)</td>
</tr>
</tbody>
</table>

The morphology of the films was investigated by SEM in Figure 2.7. The particle sizes were found to be ca. 2 µm at 450 °C. A densely packed morphology for PtSe₂ grown at T growth = 400 °C (Figure 2.7a) with a less dense morphology was observed at
higher temperatures, $T_{\text{growth}} = 450 \, ^{\circ}\text{C}$ (Figure 2.7c). The particles grown at both temperatures have a ribbon-like shape, with uniform coverage.

Figure 2.7 SEM images of PtSe$_2$ films grown at 400 °C, (a) top view, (b) Cross view and 450 °C (c) top view (d) Cross view
2.4.6 The TGA analysis of \([\text{Pd}\{\text{N}(\text{Pr}_2\text{PSe})_2\}]_2\)

The TGA curve shows that the complexes decomposed between \(ca.\ 320-373 \, ^\circ\text{C}\) (Figure 2.8) with a weight loss of 90 \%, leaving 10 \% residue which corresponds to the theoretical calculated Pd(12 \%, Table 2.12).

![Figure 2.8 TGA curve of \([\text{Pd}\{\text{N}(\text{SePr}_2\text{Pr})_2\}]_2\)](image)

2.4.7 Growth of palladium selenide thin films from \([\text{Pd}\{\text{N}(\text{Pr}_2\text{PSe})_2\}]_2\)

The precursor is highly volatile which makes it suitable for LP-MOCVD and AACVD techniques. LP-MOCVD of palladium sulfide thin films were deposited at various growth temperatures between 400-475 \(^\circ\text{C}\) at a fixed precursor temperature of 345 \(^\circ\text{C}\). XRD shows that the films grown from \([\text{Pd}\{\text{N}(\text{Pr}_2\text{PSe})_2\}]_2\] were found to be different phases of palladium selenide films depending on the growth temperatures, orthorhombic \text{PdSe}_2 (JCPDS 11-0453)\(^{174}\) at 425 \(^\circ\text{C}\), cubic \text{Pd}_{17}\text{Se}_{15} (JCPDS 29-1437)\(^{174}\) at 450 \(^\circ\text{C}\), and tetragonal \text{Pd}_4\text{Se} (JCPDS 11-0498)\(^{174}\) at 475 \(^\circ\text{C}\). XRD peaks are
indicated in Figure 2.9-2.11. Table 2.8 summarises palladium sulphide with their different phases.

**Table 2.8: XRD data of palladium chalcogenide thin films**

<table>
<thead>
<tr>
<th></th>
<th>PdSe&lt;sub&gt;2&lt;/sub&gt;-JCPDS (11-0453)</th>
<th></th>
<th>Pd&lt;sub&gt;3&lt;/sub&gt;Se&lt;sub&gt;4&lt;/sub&gt;-JCPDS (11-0498)</th>
<th></th>
<th>Pd&lt;sub&gt;17&lt;/sub&gt;Se&lt;sub&gt;15&lt;/sub&gt;-JCPDS (29-1437)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hkl</td>
<td>d(lit)/Å (% I)</td>
<td>d(exp)/Å (% I)</td>
<td>hkl</td>
<td>d(lit)/Å (% I)</td>
<td>d(exp)/Å (% I)</td>
</tr>
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<td>111</td>
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<td>4.83 (87)</td>
<td>430</td>
<td>2.12 (11)</td>
<td>2.05 (7)</td>
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<tr>
<td>102</td>
<td>3.19 (80)</td>
<td>4.01 (30)</td>
<td>511</td>
<td>2.04 (81)</td>
<td>1.90 (50)</td>
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<td>200</td>
<td>2.87 (60)</td>
<td>3.61 (33)</td>
<td>441</td>
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<tr>
<td>021</td>
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<td>3.42 (31)</td>
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</tr>
<tr>
<td>131</td>
<td>1.79 (80)</td>
<td>2.26 (22)</td>
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<td></td>
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<tr>
<td>310</td>
<td>3.35 (50)</td>
<td>3.35 (57)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>311</td>
<td>3.19 (100)</td>
<td>3.20 (83)</td>
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<td></td>
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<tr>
<td>410</td>
<td>2.57 (70)</td>
<td>2.57 (56)</td>
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<tr>
<td>330</td>
<td>2.50 (35)</td>
<td>2.49 (40)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>511</td>
<td>2.04 (81)</td>
<td>2.04 (54)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>600</td>
<td>1.77 (35)</td>
<td>2.07 (26)</td>
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</table>
Figure 2.9 XRD patterns of Pd₄Se at 475 °C

Figure 2.10 XRD patterns of PdSe₂ at 425 °C
Figure 2.11 XRD patterns of Pd$_{17}$Se$_{15}$ at 450 °C

Analysis of the film by SEM shows poor morphologies at 450 °C (Figure 2.12a, b). The films deposited were black in color and adhered well to the glass substrates. A defined platelet-like morphology was formed at $T_{\text{substrate}} = 475$ °C (Figure 2.12c). No images were obtained on films obtained at 425 °C.
Figure 2.12 SEM images of PdSe$_2$ films grown at 450 °C, (a) top view, (b) Cross view and at 475 °C, (c) top view
2.4.8 The TGA analysis of [Pt\{N(SpPr2)2\}]2

The TGA curve shows that the complex decomposed between ca. 263 °C - 369 °C (Figure 2.13) with a weight loss of 93 %, leaving 7 % residue which corresponds to the theoretical calculated PtS2(8 %, Table 2.12).

![Figure 2.13 TGA curve of [Pt\{N(SpPr2)2\}]2](image)

2.4.9 Growth of PtS2 thin films from [Pt\{N(SpPr2)2\}]2

Thin films were deposited between 300-500 °C for both the AACVD and LP-MOCVD. A polycrystalline platinum film was obtained at 450 °C by LP-MOCVD.

The EDAX confirms the presence of platinum and sulphur in 1:1 ratio. The fact that only platinum film is deposited rather than PtS2 has to do with the relatively weak coordination of platinum to sulphur in the precursor molecule. The XRD pattern shows a cubic platinum film (JCPDS 04-0802) at 450 °C (Figure 2.14).
Both the LP-MOCVD and AACVD give only the platinum films with the best film obtained at substrate temperature of 450 °C and precursor temperature of 325 °C by LP-MOCVD. The XRD patterns show no evidence of the presence of elemental sulphur. As the growth temperature increases, the platinum film becomes less crystalline as indicated by the intensity of the peaks.

Table 2.9 XRD data of platinum thin films

<table>
<thead>
<tr>
<th>hkl</th>
<th>d(lit)/Å (% I)</th>
<th>d(exp)/Å (% I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>2.45 (16)</td>
<td>1.20 (87)</td>
</tr>
<tr>
<td>200</td>
<td>1.96 (53)</td>
<td>1.96 (36)</td>
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<tr>
<td>220</td>
<td>1.39 (31)</td>
<td>1.38 (18)</td>
</tr>
<tr>
<td>311</td>
<td>1.18 (33)</td>
<td>1.18 (20)</td>
</tr>
</tbody>
</table>
The SEM images show spherical grains arranged in a reasonably uniform array on the substrate surface with particle size of ca. 2-3 μm in diameter (Figure 2.15). There appears to be a reasonable degree of depth to the coating as indicated by the SEM image. The films have a poor morphology probably as a result of evaporation of platinum and sulphur from the surface of the film.
Figure 2.15 SEM micrographs of Pt thin film from [Pt{N(S^Pr)_{2}}_{2}] at 450 °C, (a) top view, (b) Cross view
2.4.10 The TGA analysis of [Pd{N(SI"Pr₂)₂}₂]

The TGA curve shows that the precursor was highly volatile decomposed at 280-376 °C (Table 2.12).

2.4.11 Growth Pd₁₆S₇ thin films from [Pd{N(SI"Pr₂)₂}₂]

LP-MOCVD was used to deposit thin films of palladium sulphide between 300-500 °C. Energy dispersive X-ray (EDAX) analyses of the films shows that the film is rich in phosphorus, consisting of 36 % phosphorus, 2 % sulphur and 62 % palladium. A trace of phosphorus is incorporated during the decomposition of the precursor. The XRD pattern shows that the film deposited is cubic PdS₂ (JCPDS 11-0497), which is crystalline at a growth temperature of 500 °C (Figure 2.16).

Table 2.10: XRD data of PdS₂ thin films

<table>
<thead>
<tr>
<th>hkl</th>
<th>d(lit)/Å (% I)</th>
<th>d(exp)/Å (% I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>021</td>
<td>2.90 (30)</td>
<td>3.24 (92)</td>
</tr>
<tr>
<td>210</td>
<td>3.65 (60)</td>
<td>3.07 (85)</td>
</tr>
<tr>
<td>211</td>
<td>2.20 (100)</td>
<td>2.92 (67)</td>
</tr>
<tr>
<td>113</td>
<td>1.98 (60)</td>
<td>2.67 (46)</td>
</tr>
<tr>
<td>023</td>
<td>1.82 (60)</td>
<td>2.33 (68)</td>
</tr>
</tbody>
</table>

AACVD was also attempted between 300-500 °C. The same phase of PdS₂ was obtained at 425 °C and 450 °C but with a poor crystallinity.
Figure 2.16 XRD pattern of PdS$_2$ film deposited from [Pd\{N(SiPr$_2$)$_2$\}]$_2$

As the growth temperature increases to 475 °C and 500 °C the sulphur peak disappeared and the XRD shows only palladium peaks. This approach enables a comparison to be made of the different techniques to deposit the same materials from the same precursors.
Figure 2.17 SEM micrographs of PdS$_2$ thin film from [Pd{N(SiPr)$_2$}] at 500 °C (a) top view, (b) Cross view.

The SEM images (Figure 2.17) of PdS$_2$ thin film grown at 500 °C shows that the film has featureless nanocrystalline morphology on the glass substrate and is densely
packed. Oriented platelets 1.5 μm in diameter, which are fairly densely packed. The cross view SEM image shows that the platelets are densely packed and of uniform length.

2.4.12 The TGA analysis of [Pd{N(SePPh₂)₂}₂]

The TGA curve shows that the complex decomposes between ca. 274-393 °C having a weight loss 76 %, leaving 24 % residue which corresponds to the theoretically calculated PdSe(22 %, Table 2.12).

2.4.13 Growth Pd₁₇Se₁₅ thin films from [Pd{N(SePPh₂)₂}₂]

Attempts to grow thin films by LP-MOCVD proved unsuccessful. This might be due to its low volatility and higher residue observed on TGA analyses that might have resulted in a decomposed product in the precursor chamber. AACVD was also attempted to give Pd₁₇Se₁₅ (JCPDS 29-1437) thin films. They were deposited at various growth temperatures between 400-475 °C maintaining the precursor temperature at 290 °C.

Figure 2.18 XRD pattern of Pd₁₇Se₁₅ from [Pd{N(SePPh₂)₂}₂]
The XRD patterns indicated the film to have poor crystallinity (Figure 2.18). The XRD pattern showed a broad hump at $2\theta = 22^\circ$, indicating the amorphous nature of the film. The broad peak also indicates the poorly formed crystals.

2.4.14 The TGA analysis of [Pd{N(SPh$_2$)$_2$}]$_2$

TGA curve shows that the complex decomposed at between ca. 298 - 386 °C having a weight loss of approximately 75 % (Table 2.12). Residue from the decomposition of this complex is PdS$_2$ (total % = 75 + 17 = 92 %), which is close to 100 %.

2.4.15 Growth PdS thin films from [Pd{N(SPh$_2$)$_2$}]$_2$

LP-MOCVD of [Pd{N(SPh$_2$)$_2$}]$_2$ was carried out and proved unsuccessful. This might also be due to the low volatility of the precursor as indicated by TGA.

Figure 2.19 XRD pattern of PdS film deposited from [Pd{N(SPh$_2$)$_2$}]$_2$

AACVD was also attempted showing only low deposition on the glass substrates. The
precursor is slightly soluble in toluene and THF that makes it difficult to deposit thin films. Pyrolysis of the precursor was also carried out at 600 °C.

The XRD shows a crystalline orthorhombic phase of PdS (Figure 2.19). The hump at the low angle is due to diffraction from the glass substrate.

Table 2.11: XRD data of PdS thin films

<table>
<thead>
<tr>
<th>hkl</th>
<th>d(lit)/Å (% I)</th>
<th>d(exp)/Å (% I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>201</td>
<td>2.89 (74)</td>
<td>2.88 (87)</td>
</tr>
<tr>
<td>112</td>
<td>2.67 (48)</td>
<td>2.66 (73)</td>
</tr>
<tr>
<td>212</td>
<td>2.17 (11)</td>
<td>2.24 (48)</td>
</tr>
<tr>
<td>312</td>
<td>1.73 (30)</td>
<td>1.74 (32)</td>
</tr>
</tbody>
</table>

Energy dispersive X-ray (EDAX) analyses of the thin film show that it was rich in phosphorus, consisting of 30 % phosphorus, 7 % sulphur, 51 % oxygen and 11 % palladium. Phosphorus is incorporated during the decomposition of the precursor.

2.4.16 The TGA analysis of [Pt{N(SePPh2)2}]2

The TGA curve shows that the complex decomposed between ca. 254–484 °C with a weight loss 53 % (Table 2.12).

2.4.17 Growth of PtSe2 thin films from [Pt{N(SePPh2)2}]2

LP-MOCVD was done between 300–475 °C. No films were obtained at this temperature range. This is due to low volatility of the precursor leaving a large amount of residue. AACVD was done between 300-550 °C.
Four peaks were detected: a strong reflection at (100), (101) and two minor planes at (102) and (003) which corresponds to hexagonal PtSe$_2$ structure in Figure 2.20.

![XRD pattern of PtSe$_2$ from [Pt{N(SePPh$_2$)$_2$}]$_2$](image)

**Figure 2.20** XRD pattern of PtSe$_2$ from [Pt{N(SePPh$_2$)$_2$}]$_2$

Analyses of the as-deposited films show that only one phase of PtSe$_2$ (JCPDS 18-0970) thin films at 475 °C was deposited.

Less crystalline films were obtained at temperatures below and above 475 °C. There was a distinct increase in grain size (actual size) as the temperature of deposition was increased (Fig. 2.21a and 2.21c). A dense but uneven morphology was observed in both films. The average grain size is 0.5 μm.
Figure 2.21 SEM micrographs of PtSe$_2$ thin film from [Pt{N(SePPh$_2$)$_2$}] at 450 °C.
(a) top view, (b) Cross view and at 475 °C (c) top view, and (d) cross view.

Viewing the images sequentially, we could observe that as the temperature increased, the size of the grains increased.
2.4.18 The TGA analysis of \([\text{Pt}\{\text{N(SPh}_2\}_2}\]_2\)

The TGA curve shows that the complexes decomposed between *ca.* 317–467 °C with a weight loss of approximately 72 %, leaving 28 % residue which corresponds to the theoretical calculated Pt(24 %, Table 2.12).

2.4.19 Growth PtS thin films from \([\text{Pt}\{\text{N(SPh}_2\}_2]\]_2\)

LP-MOCVD proved unsuccessful due to the low volatility of the precursor. AACVD was also carried out at various temperatures. The XRD showed poor crystallinity of the Pt (JCPDS 04-802) thin films (Figure 2.22). AACVD was done but the precursor was partially soluble in toluene and THF.

![Figure 2.22 XRD pattern of Pt thin film deposited from [Pt{N(SPh2)}2]2](image)

No peaks corresponded to PtS; this indicates that the as-deposited films are either amorphous or contain a small amount of crystalline phase. The XRD pattern matches well with the literature data for the cubic phase of platinum.⁹⁷
Energy dispersive X-ray (EDAX) analyses of the powder shows that it was rich in phosphorus, consisting of 34% phosphorus, 21% sulphur, 35% oxygen and 8% platinum. EDAX indicated the presence of sulphur which contradicted the XRD patterns.

2.4.20 The TGA analysis of [Ni{N(Se\text{P}Pr\text{$_2$})$_2$}]$_2$

The TGA curve shows the initial decomposition at ca. 195°C. The second major decomposition occurs between ca. 300-328°C having a weight loss of 77%, leaving 23% residue which correspond to the theoretical calculated NiSe$_2$(26%, Table 2.12). The TGA curve indicates that this precursor is supposed to be good for deposition of thin films.

2.4.21 Growth of NiSe$_2$ thin films from [Ni{N(Se\text{P}Pr\text{$_2$})$_2$}]$_2$

Growth of the thin films by both LP-MOCVD and AACVD were attempted. No deposition was obtained between 300-500°C using LP-MOCVD. AACVD was done between 300-500°C. Little deposition was obtained at 450°C. No images were observed on SEM.

2.4.22 The TGA analysis of [Ni{N(Se\text{P}Pr\text{$_2$})$_2$}]$_2$

The TGA indicate initial decomposition at ca. 187°C (Table 2.12).

2.4.23 Growth of NiS$_2$ thin films from [Ni{N(Se\text{P}Pr\text{$_2$})$_2$}]$_2$

Again no deposition was obtained between 300-500°C using LP-MOCVD and AACVD.
2.4.24 The TGA analysis of [Ni{N(SPPh$_2$)$_2$}]$_2$

The TGA curve shows that the precursor decomposed between ca. 347-389 °C with a weight loss of 64 %(Table 2.12).

2.4.25 Growth of NiS$_2$ thin films by [Ni{N(SPPh$_2$)$_2$}]$_2$

No deposition was obtained between 300-500 °C using LP-MOCVD and AACVD.

2.4.26 The TGA analysis of [Ni{N(SePPh$_2$)$_2$}]$_2$

The TGA curve show that the precursor decomposed between ca. 308-401 °C with a weight loss of 64 %(Table 2.12).

2.4.27 Growth of NiSe$_2$ thin films from [Ni{N(SePPh$_2$)$_2$}]$_2$

No deposition was obtained between 300-500 °C in both LP-MOCVD and AACVD.

This is due to the low volatility of the precursor.
Table 2.12 The TGA data of $[\text{M} \{\text{N} \left( \text{EPR}_2 \right) \}_2]$, $\text{E} = \text{S or Se}$, $\text{R} = \text{Ph or ^1Pr}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>% loss(0-500 °C)</th>
<th>Experimental % residue</th>
<th>Theoretical % residue</th>
<th>nature of residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Pt} {\text{N(SeP^1Pr}_2 }_2]$</td>
<td>87</td>
<td>13</td>
<td>Pt(19 %)</td>
<td></td>
</tr>
<tr>
<td>$[\text{Pt} {\text{N(SP^1Pr}_2 }_2]$</td>
<td>93</td>
<td>7</td>
<td>PtS_2(8 %)</td>
<td></td>
</tr>
<tr>
<td>$[\text{Pd} {\text{N(SeP^1Pr}_2 }_2]$</td>
<td>90</td>
<td>10</td>
<td>Pd(12 %)</td>
<td></td>
</tr>
<tr>
<td>$[\text{Pd} {\text{N(SP^1Pr}_2 }_2]$</td>
<td>99</td>
<td>1</td>
<td>Pd(15 %)</td>
<td></td>
</tr>
<tr>
<td>$[\text{Pd} {\text{N(SePPPh}_2 }_2]$</td>
<td>76</td>
<td>24</td>
<td>PdSe_2(22 %)</td>
<td></td>
</tr>
<tr>
<td>$[\text{Pd} {\text{N(SPPPh}_2 }_2]$</td>
<td>75</td>
<td>25</td>
<td>PdS_2(17 %)</td>
<td></td>
</tr>
<tr>
<td>$[\text{Pt} {\text{N(SePPPh}_2 }_2]$</td>
<td>53</td>
<td>47</td>
<td>PtSe_2(28 %)</td>
<td></td>
</tr>
<tr>
<td>$[\text{Pt} {\text{N(SPPPh}_2 }_2]$</td>
<td>72</td>
<td>28</td>
<td>PtS_2(24 %)</td>
<td></td>
</tr>
<tr>
<td>$[\text{Ni} {\text{N(SeP^1Pr}_2 }_2]$</td>
<td>77</td>
<td>23</td>
<td>NiSe_2(26 %)</td>
<td></td>
</tr>
<tr>
<td>$[\text{Ni} {\text{N(SP^1Pr}_2 }_2]$</td>
<td>101</td>
<td>-</td>
<td>NiS(13 %)</td>
<td></td>
</tr>
<tr>
<td>$[\text{Ni} {\text{N(SPPPh}_2 }_2]$</td>
<td>64</td>
<td>36</td>
<td>NiS_2(13 %)</td>
<td></td>
</tr>
<tr>
<td>$[\text{Ni} {\text{N(SePPPh}_2 }_2]$</td>
<td>64</td>
<td>36</td>
<td>NiSe_2(19 %)</td>
<td></td>
</tr>
</tbody>
</table>

2.5 Conclusions

Compounds of the type $[\text{M} \{\text{N} \left( \text{EPR}_2 \right) \}_2]$, $\text{M} = \text{Pt(II), Pd(II); R} = \text{^1Pr, Ph}_2$ and $\text{E} = \text{S, Se}$ were used as single source precursors for the deposition of metal chalcogenide thin films via a low-pressure metal-organic chemical vapour deposition (LP-MOCVD) and aerosol assisted chemical vapour deposition (AACVD). The X-ray structures of $[\text{Pt} \{\text{N(SeP^1Pr}_2 \}_2]$ and $[\text{Pd} \{\text{N(SPPPh}_2 \}_2]$ were obtained. The structures are square-
planner geometry with the six membered PtSe$_2$-P$_3$N rings adopting a distorted “boat” conformation. The structure is not similar to the one reported by Cupertino et al.$^{79}$.

All the complexes were characterised by elemental analysis, IR, MS, $^1$H and $^{13}$C NMR. Thin films of PtSe$_2$, Pt, PdSe$_2$, Pd$_{17}$Se$_{15}$, and PdS$_2$ were deposited by AACVD and LPMOCVD techniques. The morphology, crystallinity and stoichiometry were investigated by XRD, SEM, and EDAX. Polycrystalline PtSe$_2$ (hexagonal) films were grown between 400 - 450 °C from [Pt{N(SeP$_3$Pr$_2$)$_2$}] and crystallinity increases with temperature as indicated by the intensity of the peaks {001(a), (b), (c)}. A strong XRD peak was observed at 18.20° (001) in all the samples followed by two minor peaks at 32.5° (101) and 55.30° (200). The ribbon-like densely packed morphology with average particle size of ca. 2 μm at 400 °C and less dense morphology at 450 °C was obtained. Pt (cubic) instead of PtS$_2$ film was obtained due to weak coordination of Pt to S in the precursor molecule. Spherical grains with average particle size of ca. 2-3 μm in diameter. Different phases of palladium selenide were obtained depending on temperature. Platelet-like morphology was obtained. The R group (isopropyl or phenyl) plays an important role in the decomposition, crystallinity and stoichiometry of the materials.

The type of the ligand plays an important role to control the stoichiometry of the as-deposited films and in some cases may provide routes for the growth of specific phases. Much scope remains for the development of these precursors for lower deposition temperatures and well defined phases. No depositions were observed using nickel complex even though they show one stage decomposition by TGA. Using LP-MOCVD, the reason might be that the settings of vapour pressure were not done properly.
Chapter 3

Deposition of metal sulphide thin films from xanthate precursors
3.1 Introduction

Xanthates (o-ethyldithiocarbonates) were first discovered by Zeise\textsuperscript{106} in 1822. They have been used by industry as floatation agents for the thiophilic minerals of the transition metals such as copper, zinc, cobalt, nickel and gold, separation and quantitative determination of a larger number of cations and trifluoroethylxanthate has been used as a reagent for the analytical determination of gold\textsuperscript{106-107}. Xanthate and dithiocarbamates ligands have been studied recently due to their structural similarities.

\[ \text{RO-C \rightleftharpoons S} \]
\[ \text{R}_2\text{N-C \rightleftharpoons S} \]

Xanthate

Dithiocarbamate

\( R = \text{alkyl or aryl} \)

Xanthates are usually prepared by mixing an alcohol with potassium hydroxide and carbon disulfide (equation 3.1).

\[ \text{KOR} + \text{CS}_2 \rightarrow \text{ROCS}_2\text{K} \quad \text{eq. 3.1} \]

Xanthate ligands can act as monodentate, bidentate or bridging to two or even three metal centers with sulphur, which lead to a variety of complexes.
The transition metal xanthates have been extensively studied for their broad applications in industry. Metal xanthates have been prepared previously to determine their composition and structure. The metal is located at a center of inversion, is coordinated by two equivalent xanthate groups, each group behaving as a bidentate ligand through the two sulphur atoms.

\[
\text{RO-C=S=S-M-C-OR}
\]

Metal alkyl xanthate, R = alkyl or aryl; M = Cd, Zn, Pd, Pt, As, Sb and Bi.\textsuperscript{108-115}

Metal-xanthate complexes have low solubility products and high stability constants, and therefore xanthates exhibit high efficacy for the removal of metal ions.

Cheon, \textit{et al.}\textsuperscript{116} have reported deposition of NiS and PdS thin films from both a thermal and photochemical CVD route using single-source precursors of the type \(\text{M(S_2COCHMe}_2\text{)}_2\), \(\text{M = Ni and Pd}\). O’Brien, \textit{et al.}\textsuperscript{117} have recently reported the deposition of binary nickel sulfide films from nickel complexes of various alkyl dithiocarbamate derivatives nickel using a low-pressure metal-organic chemical vapour deposition technique. The morphology of the films was shown to be predominantly in the shape of wires. NiS nanowhiskers have also been reported by reacting a nickel substrate and sulfur in ethylenediamine.\textsuperscript{118} The authors report a change of morphology and composition with variation in reaction conditions.
Nickel sulfide has been studied because of its potential as a transformation toughening agent for materials used in semiconductor applications. Their uses as catalysts and coatings for photogalvanic cells have also been reported. The existence of various compositions of nickel sulfide including \( \text{Ni}_{3+x}S_2 \), \( \text{Ni}_3S_2 \), \( \text{Ni}_4S_3+x \), \( \text{Ni}_8S_5 \), \( \text{Ni}_7S_6 \), \( \text{Ni}_9S_8 \), \( \text{NiS} \), \( \text{Ni}_3S_4 \) and \( \text{NiS}_2 \) makes such studies both interesting and challenging.\(^{116,118}\)

Cadmium chalcogenide thin films are useful materials in solid-state solar cells, photoconductors, field effect transistors, sensors, and transducers. The morphology and microstructure of polycrystalline CdS films are major concern in the fabrication process of CdTe solar cells. Afzaal, et al.\(^{119-120}\) reported the deposition of CdS and CdSe by LP_MOCVD using \([\text{Cd}\{\text{N}(\text{EPPr}_2)\}_2]\) , \((\text{E} = \text{S}, \text{Se})\) as single source precursors.

Yellow, transparent, and well-adherent to the glass surface CdS thin films were grown at growth temperature of \(425\ \degree\text{C}\) and \(450\ \degree\text{C}\). At \(475\ \degree\text{C}\), slightly dark yellow-brown films were obtained. Analysis of the as-deposited films show that hexagonal phase of CdS (JCPDS-06-0314) is prepared, regardless of difference in growth temperature. XRD pattern show a preferred orientation along the (002) plane independent of growth temperature. At higher temperature \(475\ \degree\text{C}\) the film were found to be amorphous. SEM indicate that the morphology of the film at \(450\ \degree\text{C}\) consist of randomly oriented domains of compacted thin acicular crystallites and the film thickness to be \(1.75\ \mu\text{m}\) thick. EDAX analysis, the films was found to be slightly cadmium rich (52 \%) and also, 2 \% of phosphorus was detected.

Sebastian, et al.\(^{121}\) deposited both intrinsic CdS and n-CdS, which exhibited hexagonal Greenockite structure, with a preferred orientation along (002) for n-CdS.
Deposition of Metal sulphide thin films from xanthate precursors

Meyer, et al.\textsuperscript{122} deposit both undoped and In-doped films of CdS. The SEM of CdS shows a columnar microstructure, low porosity and good adherence to the substrate. Barreca, et al.\textsuperscript{123} prepared ZnS and CdS thin films using M(O-i-Pr Xan)\textsubscript{2} [M = Zn, Cd; O-i-PrXan = S\textsubscript{2}COCH(CH\textsubscript{3})\textsubscript{2}] as single source precursors. All the CdS reported exhibit a hexagonal phase by XRD. SEM shows a smooth and regular surface morphology.

3.2 Experimental

3.2.1 Materials and methods

All chemicals used were of analytical grade quality and were used without further purification. Deionised water was used for all experimental work. Ethylxanthic acid, potassium salt, o-isopropylxanthic acid, potassium salt, methanol, potassium tetrachloroplatinate(II), potassium tetrachloropalladate(II), cadmium(II)chloride; and cobalt hexahydrate, cobalt(II)chloride (98 %, Fluka Chemika), copper(II)nitrate hydrate (95 %, BDH), cadmium chloride anhydrous, cadmium chloride (99 %, Aldrich).

3.2.2 Preparation of metal xanthate precursors

Metal alkylxanthate compounds, [M(S\textsubscript{2}COR)\textsubscript{2}], M = Ni, Pt, Pd, Cd, Co and Cu; R = Et or i-Pr were prepared by stoichiometric reaction of potassium alkylxanthate and metal salts following the literature procedure.\textsuperscript{108} All reactions were carried out at room temperature.
3.2.2.1 Synthesis of [Ni(S2COR)2], R = Et or iPr.

A methanolic solution of NiCl2·6H2O (0.371 g, 1.56 mmol, 10 mL) was added to C2H5OCS2K (0.5 g, 3.12 mmol) in methanol (10 mL). Brown solution was obtained which turns blue after 15 min. The metal xanthate forms rapidly and precipitates. The reaction mixture was stirred for 1 h. The mixture was filtered and washed three times with water (3 x 10 mL) followed by methanol (3 x 10 mL). The resulting metal dixanthate was dried at room temperature in air. Yield: 0.75 g, 80 %. MP = 142 °C. [Ni(C2H5OCS2)2] : Microanalysis: Anal. Caled. for C11H10O2NiS4: C, 23.93; H, 3.35; S, 42.60. Found: C, 23.80; H, 3.27; S, 42.75. 1H NMR (CDCl3) ordered as δ(ppm), multiplicity, relative ratio, assignment; 4.65 (q, 2H, S2COCH2CH3); 1.45 (t, 3H, S2COCH2CH3). 13C NMR (CDCl3) ordered as δ(ppm), 68.75 (S2COCH2CH3), 14.01 (S2COCH2CH3). MS: m/z = 301 correspond to [M + H]+.

Similar procedure was used to prepare [Ni(C3H7OCS2)2]. Except that 0.0682 g (0.287 mmol, 10 mL) of NiCl2·6H2O and 0.1 g (0.574 mmol) in methanol (10 mL) of C3H7OCS2K were used. Yield: 0.74 g, 74 %. MP = 120 °C. [Ni(C3H7OCS2)2] : Microanalysis: Anal. Caled for C13H14O2NiS4: C, 29.19; H, 4.29; S, 38.97. Found: C, 29.32; H, 4.19; S, 38.75. 1H NMR (CDCl3) ordered as δ (ppm), multiplicity, relative ratio, assignment, 1.5 ppm [d, 6H, S2COCH(CH3)2]; 1.48 [q, 1H, S2COCH(CH3)2]. MS: m/z = 329 corresponds to [M + H]+.

3.2.2.2 Synthesis of [Pd(S2COR)2], R = Et or iPr

An aqueous solution of K2PdCl4 (0.102 g, 0.312 mmol, 10 mL) was added to C2H5OCS2K (0.1 g, 0.624 mmol) in methanol (10 mL). The mixture turns yellow immediately. The reaction mixture was stirred for 1 h. The mixture was filtered and
Deposition of Metal sulphide thin films from xanthate precursors

washed three times with water (3 x 10 mL) and then with methanol (3 x 10 mL). The resulting metal dixanthate was dried at room temperature in air. Yield: 0.085 g, 78 %.

MP = 153 °C. [Pd(C2H5OCS2)2]: Microanalysis: Anal. Calcd for C6H10O2PdS4: C, 25.50; H, 3.74; S, 34.03. Found: C, 25.55; H, 3.66; S, 34.70. 1H NMR (CDCl3) ordered as δ(ppm), multiplicity, relative ratio, assignment; 4.68 (q, 2H, S2COCH2CH3); 1.60 (t, 3H, S2COCH2CH3). 13C NMR (CDCl3) ordered as δ(ppm), 68.75 (S2COCH2CH3), 14.01 (S2COCH2CH3).

[Pd(C3H7OCS2)2] was prepared by similar procedure using 0.0936 g (0.287 mmol, 10 mL) of K2PdCl4 and 0.1 g (0.574 mmol) of C3H7OCS2K in methanol solution (10 mL). A yellow precipitate was formed immediately. Yield: 0.075 g, 69 %. MP = 144 °C. [Pd(C3H7OCS2)2]: Microanalysis: Anal. Calcd for C8H14O2PdS4: C, 25.50; H, 3.73; S, 34.03. Found: C, 25.55; H, 3.66; S, 34.70. 1H NMR (CDCl3) ordered as δ(ppm), multiplicity, relative ratio, assignment; 1.5 ppm [d, 6H, S2COCH(CH3)2]; 1.48 [q, 1H, S2COCH(CH3)2]. MS: m/z = 329 correspond to [M + H]+.

3.2.2.3 Synthesis of [Pt(S2COR)2], R = Et or iPr.

An aqueous solution of K2PtCl4 (0.13 g, 0.312 mmol, 10 mL) was added to C2H5OCS2K (0.1 g, 0.624 mmol) in methanol (10 mL). The reaction mixture was stirred for 1 h. A yellow precipitate was formed. The mixture was vacuum filtered and washed three times with a water (3 x 10 mL) and then with methanol (3 x 10 mL). The yellow product was dried at room temperature in air. Yield: 0.46 g, 65 %. MP = 130 °C. [Pt(C2H5OCS2)2]: Microanalysis: Anal. Calcd. for C8H10O2PtS4: C, 16.47; H, 2.30; S, 29.32. Found: C, 16.47; H, 2.03; S, 29.08.
Similar procedure was used to prepare \([\text{Pt}(C_2H_7OCS_2)_2]\) using 0.12 g (0.287 mmol, 10 mL) of \(K_2\text{PtCl}_4\) and 0.1 g (0.574 mmol) of \(C_3H_7OCS_2K\) in methanol (10 mL). The resulting platinum dixanthate complex was dried at room temperature in air. Yield: 0.088 g, 66 %. MP = 140 °C. \([\text{Pt}(C_3H_7OCS_2)_2]\) : Microanalysis: Anal. Calcd. for \(C_4H_{14}O_2PtS_4\): C, 20.64; H, 3.03; S, 27.55. Found: C, 20.65; H, 2.93; S, 27.92.

### 3.2.2.4 Synthesis of \([\text{Cd}(S_2COR)_2]\), R = Et or \(^1\text{Pr}\).

An aqueous solution of \(\text{CdCl}_2\) (0.0571 g, 0.312 mmol, 10 mL) was added to \(C_2H_5OCS_2K\) (0.1 g, 0.624 mmol) in methanol (10 mL). A white precipitate was formed immediately. The reaction mixture was stirred for 1 h. The mixture was vacuum filtered and washed three times with water (3 x 10 mL) and then with methanol (3 x 10 mL). The white product was dried at room temperature in air. Yield: 0.095 g, 86 %. MP = 165 °C. \([\text{Cd}(C_2H_5OCS_2)_2]\) : Microanalysis: Anal. Calcd for \(C_6H_{10}O_2CdS_4\): C, 20.31; H, 2.84; S, 36.15 Found: C, 20.25; H, 2.55; S, 35.72. \(^1\text{H}\) NMR (CDCl\(_3\)) ordered as \(\delta(\text{ppm})\), multiplicity, relative ratio, assignment; 4.41 (q, 2H, \(S_2COCH_2CH_3\)); 1.39 (t, 3H, \(S_2COCH_2CH_3\)). MS: \(m/z = 353\) correspond to \([M + H]^+\).

A similar procedure was used to prepare \([\text{Cd}(C_3H_7OCS_2)_2]\) using 0.053 g (0.287 mmol, 10 mL) of \(\text{CdCl}_2\) and 0.1 g (0.574 mmol) of \(C_3H_7OCS_2K\) in methanol (10 mL). Yield: 0.098 g, 89 %. MP = 173 °C. \([\text{Cd}(C_3H_7OCS_2)_2]\): Microanalysis: Anal. Calcd for \(C_8H_{14}O_2CdS_4\): C, 25.10; H, 3.69; S, 33.50 Found: C, 25.32; H, 3.56; S, 33.91.
3.2.2.5 Synthesis of $[\text{Co(S}_2\text{COR})_2]$, $\text{R} = \text{Et}$ or $\text{iPr}$.

An aqueous solution of $\text{CoCl}_2\cdot6\text{H}_2\text{O}$ (0.07 g, 0.312 mmol, 10 mL) was added to $\text{C}_2\text{H}_5\text{OCS}_2\text{K}$ (0.1 g, 0.624 mmol) in methanol (10 mL). A black precipitate started to form immediately. The reaction mixture was stirred for 1 h. The mixture was vacuum filtered and washed three times with water (3 x 10 mL) and then with methanol (3 x 10 mL). The resulting cobalt dixanthate complex was dried at room temperature in air. Yield: 0.075 g, 80 %. M.P. = 123 °C. $[\text{Co(C}_2\text{H}_5\text{OCS}_2)_2]$ : Microanalysis: Anal. Calcd for $\text{C}_9\text{H}_{10}\text{O}_2\text{CoS}_4$: C, 23.91; H, 3.34; S, 42.56. Found: C, 22.03; H, 3.33; S, 41.09.

A similar procedure was used to prepare $[\text{Co(C}_3\text{H}_7\text{OCS}_2)_2]$ using 0.0682 g (0.287 mmol, 10 mL) of $\text{CoCl}_2\cdot6\text{H}_2\text{O}$ and 0.1 g (0.574 mmol) of $\text{C}_3\text{H}_7\text{OCS}_2\text{K}$ in deionised water (10 mL). Yield: 0.084 g, 89 %. M.P. = 162 °C. $[\text{Co(C}_3\text{H}_7\text{OCS}_2)_2]$ : Microanalysis: Anal. Calcd for $\text{C}_9\text{H}_{14}\text{O}_2\text{CoS}_4$: C, 20.64; H, 3.03; S, 27.55 Found: C, 20.65; H, 2.93; S, 27.92.

3.2.2.6 Synthesis of $[\text{Cu(C}_2\text{H}_5\text{OCS}_2)_2]$

An aqueous solution of $\text{Cu(NO}_3)_2$ (0.075 g, 0.312 mmol, 10 mL) was added to $\text{C}_2\text{H}_5\text{OCS}_2\text{K}$ (0.1 g, 0.624 mmol) in methanol (10 mL). The precipitate formed immediately. The reaction mixture was stirred for 1 h. The mixture was filtered and washed three times with water (3 x 10 mL) and then with methanol (3 x 10 mL). The resulting copper dixanthate complex was dried at room temperature in air. Yield: 0.085 g, 86 %. M.P. = 122 °C. $[\text{Cu(C}_2\text{H}_5\text{OCS}_2)_2]$ : Microanalysis: Anal. Calcd for $\text{C}_9\text{H}_{10}\text{O}_2\text{CuS}_4$: C, 23.55; H, 3.29; S, 41.92. Found: C, 22.55; H, 3.14; S, 41.16.
Table 3.1 Microanalysis of metal xanthate precursors

<table>
<thead>
<tr>
<th>Precursors</th>
<th>Found (calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%C</td>
</tr>
<tr>
<td>1. Ni(S₂COC₂H₅)₂</td>
<td>23.80 (23.93)</td>
</tr>
<tr>
<td>2. Pd(S₂COC₂H₅)₂</td>
<td>20.63 (20.66)</td>
</tr>
<tr>
<td>3. Pt(S₂COC₂H₅)₂</td>
<td>16.47 (16.47)</td>
</tr>
<tr>
<td>4. Co(S₂COC₂H₅)₂</td>
<td>22.03 (23.91)</td>
</tr>
<tr>
<td>5. Cd(S₂COC₂H₅)₂</td>
<td>20.25 (20.31)</td>
</tr>
<tr>
<td>6. Cu(S₂COC₂H₅)₂</td>
<td>22.55 (23.55)</td>
</tr>
<tr>
<td>7. Ni(S₂COCHMe₂)₂</td>
<td>29.32 (29.19)</td>
</tr>
<tr>
<td>8. Pd(S₂COCHMe₂)₂</td>
<td>25.55 (25.50)</td>
</tr>
<tr>
<td>9. Pt(S₂COCHMe₂)₂</td>
<td>20.65 (20.64)</td>
</tr>
<tr>
<td>10. Co(S₂COCHMe₂)₂</td>
<td>27.46 (29.17)</td>
</tr>
<tr>
<td>11. Cd(S₂COCHMe₂)₂</td>
<td>25.32 (25.10)</td>
</tr>
</tbody>
</table>
3.3 Results and discussions

3.3.1 Single X-ray structure of [Ni(S₂COEt₂)₂]

Figure 3.1 ORTEP diagram showing atomic numbering of [Ni(S₂COEt₂)₂]

Figure 3.2 Packing diagram of [Ni(S₂COEt₂)₂]
Deposition of Metal sulphide thin films from xanthate precursors

Crystals suitable for X-ray diffraction studies were obtained by slow diffusion of hexane/dichloromethane mixture. Data were collected at 100(2) K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) by Bruker APEX diffractometer. Data was collected using a Bruker-based diffractometer equipped with a LT-2 low temperature apparatus operating at 100 K.

Details of data collection and structure refinements are shown in Table 3.2.

The crystal structure of nickel xanthate has been determined by three dimensional X-ray diffraction techniques and refined by a full matrix least squares method on F².

Crystals are orthorhombic, space group pbca, Z = 4 with cell dimensions a = 7.4077(7), b = 7.0961(7), and c = 20.7565(19). Intensity data for a platelike crystal 0.70 x 0.50 x 0.20 mm were obtained. X-ray crystallography studies revealed each complex to have nickel at a center of inversion coordinated by two equivalent xanthate groups behaving as a bidentate ligand through four sulphur atoms, as shown in Figure 3.1. The packing diagram showing intermolecular Ni...S interactions is shown in Figure 3.2. The complex is similar to the one reported in the literature.¹¹
Table 3.2 Crystal data and structural refinement details for [Ni(S₂COEt₂)₂]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₆H₁₆NiO₅S₄</td>
</tr>
<tr>
<td>Formula weight</td>
<td>301.09</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal System, space group</td>
<td>Orthorhombic, pbca</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a = 7.4077(7) Å</td>
<td>90°</td>
</tr>
<tr>
<td>b = 7.0961(7) Å</td>
<td>90°</td>
</tr>
<tr>
<td>c = 20.7565(19) Å</td>
<td>90°</td>
</tr>
<tr>
<td>Volume</td>
<td>1091.08(18) Å</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>4, 1.833 mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>2.507 mm⁻¹</td>
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<tr>
<td>F(000)</td>
<td>616</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.70 x 0.50 x 0.20 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.96 to 26.38 deg</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-9 ≤ h ≤ 7, -7 ≤ k ≤ 8, -25 ≤ l ≤ 25</td>
</tr>
<tr>
<td>Reflections collected/unique</td>
<td>5655/1111 [R(int) = 0.0230]</td>
</tr>
<tr>
<td>Completeness to theta = 26.41</td>
<td>99.8%</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.6340 and 0.2728</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>1111/0/62</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.097</td>
</tr>
<tr>
<td>Final R indices [I &gt; 2 sigma (I)]</td>
<td>R1 = 0.0225, wR2 = 0.0600</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0240, wR2 = 0.0611</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.617 and -0.495 e Å⁻³</td>
</tr>
</tbody>
</table>
Table 3.3 Selected bond length (Å) and angles (deg) for [Ni(S$_2$COEt$_2$)$_2$]

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(1)–S(1)</td>
<td>2.2197(5)</td>
<td></td>
</tr>
<tr>
<td>Ni(1)–S(2)</td>
<td>2.2175(5)</td>
<td></td>
</tr>
<tr>
<td>S(1)–C(1)</td>
<td>1.7019(17)</td>
<td></td>
</tr>
<tr>
<td>S(2)–C(1)</td>
<td>1.6914(17)</td>
<td></td>
</tr>
<tr>
<td>O(1)–C(1)</td>
<td>1.308(2)</td>
<td></td>
</tr>
<tr>
<td>O(1)–C(2)</td>
<td>1.468(2)</td>
<td></td>
</tr>
<tr>
<td>C(2)–C(3)</td>
<td>1.501(2)</td>
<td></td>
</tr>
</tbody>
</table>

3.3.2 Single crystal X-ray structure of [Pd(S$_2$COEt$_2$)$_2$]

The single crystal was obtained by slow diffusion of n-hexane into a dichloromethane solution of the complex at room temperature. Interatomic distances and angles are listed in Table 3.4.

The palladium X-ray structure was previously reported. The structure reveals that it is square planar. X-ray analysis of the present structure reveals that [Pd(S$_2$COEt$_2$)$_2$], lies on an inversion center and adopts a square planar geometry defined by the four sulphur atoms of the two dithiocarbonate (xanthate) ligands. The ORTEP diagram shows the atom numbering (Figure 3.3) and the packing diagram shows intermolecular Pd...S interactions (dashed lines, Figure 3.4). Details of data collection and structure refinements are shown in Table 3.4.
Deposition of Metal sulphide thin films from xanthate precursors

Figure 3.3 ORTEP diagram showing atomic numbering of $\text{[Pd(S_2COEt_2)_2]}$

Figure 3.4 Packing diagram of $\text{[Pd(S_2COEt_2)_2]}$
Table 3.4 Crystal data and structural refinement details for [Pd(S₂CO₂Et₂)₂]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₆H₁₀PdO₂S₄</td>
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<tr>
<td>Formula weight</td>
<td>348.78</td>
</tr>
<tr>
<td>Temperature</td>
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</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal System, space group</td>
<td>Orthorhombic, pbca</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 7.465(3) Å, b = 7.166(3) Å, c = 20.678(8) Å</td>
</tr>
<tr>
<td></td>
<td>α = 90°, β = 90°, γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>1106.2(8) Å</td>
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<tr>
<td>Z, Calculated density</td>
<td>4, 2.094 mg/m³</td>
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<td>Absorption coefficient</td>
<td>2.397 mm⁻¹</td>
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<tr>
<td>F(000)</td>
<td>688</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.30 x 0.20 x 0.20 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.97 to 26.69 deg</td>
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<tr>
<td>Limiting indices</td>
<td>-9 ≤ h ≤ 8, -9 ≤ k ≤ 9, -26 ≤ l ≤ 26</td>
</tr>
<tr>
<td>Reflections collected/unique</td>
<td>7653/1162</td>
</tr>
<tr>
<td>Completeness to theta = 26.41</td>
<td>99.7%</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.6457 and 0.5333</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>1162/0/62</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.241</td>
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<tr>
<td>Final R indices [I &gt; 2 sigma (I)]</td>
<td>R1 = 0.0443, wR2 = 0.0984</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0494, wR2 = 0.1006</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.183 and -1.047 e.Å⁻³</td>
</tr>
</tbody>
</table>
Deposition of Metal sulphide thin films from xanthate precursors

Table 3.5 Selected bond length (Å) and angles (deg) for [Pd(S₂COEt₂)₂]

<table>
<thead>
<tr>
<th>Bond 1</th>
<th>Bond 2</th>
<th>Bond 3</th>
<th>Bond 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(1) – S(1)</td>
<td>2.3280(16)</td>
<td>S(1) – Pd(1) – S(1)</td>
<td>180.0(2)</td>
</tr>
<tr>
<td>Pd(1) – S(2)</td>
<td>2.3192(16)</td>
<td>S(2) – Pd(1) – S(1)</td>
<td>75.43(5)</td>
</tr>
<tr>
<td>S(1) – C(1)</td>
<td>1.692(6)</td>
<td>C(1) – S(1) – Pd(1)</td>
<td>84.6(2)</td>
</tr>
<tr>
<td>S(2) – C(1)</td>
<td>1.681(6)</td>
<td>C(1) – S(2) – Pd(1)</td>
<td>85.1(2)</td>
</tr>
<tr>
<td>O(1) – C(1)</td>
<td>1.302(7)</td>
<td>C(1) – O(1) – C(2)</td>
<td>118.1(4)</td>
</tr>
<tr>
<td>O(1) – C(2)</td>
<td>1.459(6)</td>
<td>O(1) – C(2) – C(3)</td>
<td>106.9(5)</td>
</tr>
<tr>
<td>C(2) – C(3)</td>
<td>1.493(9)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.3.3 Single X-ray structure of [Pt(S₂COEt₂)₂]

The single crystals were obtained using the same procedure as described in 3.3.2.

Selected bond lengths and angles for this complex are given in Table 3.6.

Hydrogen atoms were placed in calculated positions, assigned anisotropic thermal parameters and allowed to ride on their parent carbon atoms. The range of h, k, and l are -9 < h < = 5, -8 < k < = 9, -24 < l < = 25. Total numbers of measured and observed independent reflection are 5878 and 1163 [R (int) = 0.0320]. The final R and Rₜ values are given in the Table 3.6.
Deposition of Metal sulphide thin films from xanthate precursors

Figure 3.5 ORTEP diagram showing atomic numbering of [Pt(S₂COEt₂)₂]

Figure 3.6 Packing diagram of [Pt(S₂COEt₂)₂]
Table 3.6 Crystal data and structural refinement details for \([\text{Pt}(\text{S}_2 \text{COET}_2)_2]\)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>(\text{C}<em>6\text{H}</em>{10}\text{Pt}_2\text{S}_4)</td>
</tr>
<tr>
<td>Formula weight</td>
<td>437.47</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal System, space group</td>
<td>Orthorhombic, pbca</td>
</tr>
</tbody>
</table>
| Unit cell dimensions         | \(a = 7.6472(9) \text{ Å} \quad a = 90°\)  
                            | \(b = 7.2460(8) \text{ Å} \quad b = 90°\)  
                            | \(c = 20.523(2) \text{ Å} \quad c = 90°\)  |
| Volume                       | 1137.2(2) Å³                 |
| Z, Calculated density        | 4, 2.555 mg/m³               |
| Absorption coefficient       | 13.038 mm⁻¹                  |
| \(F(000)\)                   | 816                          |
| Crystal size                 | 0.20 x 0.20 x 0.20 mm        |
| Theta range for data collection | 1.98 to 26.40 deg           |
| Limiting indices             | \(-9 < h < 5, -8 < k < 9, -24 < l < 25\) |
| Reflections collected/unique | 5878/1163 [R (int) = 0.0320] |
| Completeness to theta = 26.41| 99.7 %                       |
| Absorption correction        | Semi-empirical from equivalents |
| Max. and min. transmission   | 0.1802 and 0.1802            |
| Refinement method            | Full-matrix least-squares on \(F^2\) |
| Data/restraints/parameters    | 1163/ 0/ 62                  |
| Goodness-of-fit on \(F^2\)   | 1.057                        |
| Final R indices [I > 2 sigma (I)] | \(R_1 = 0.0207, wR_2 = 0.0420\) |
| R indices (all data)         | \(R_1 = 0.0289, wR_2 = 0.0444\) |
| Largest diff. peak and hole  | 0.669 and -0.573 e.Å⁻³       |
The complex reveal that it is a monomeric square planar which is similar to the reported structure stoichiometrically and geometrical. The S atoms are arranged in a distorted tetrahedron with the S—Pt—S angles varying from 180 and 75°.

Table 3.7 Selected bond length (Å) and angles (deg) for [Pt(S₂COEt₂)₂]

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(1) – S(1)</td>
<td>2.3316(10)</td>
<td>S(1) – Pt(1) – S(1) 179.999(1)</td>
</tr>
<tr>
<td>Pt(1) – S(2)</td>
<td>2.3242(10)</td>
<td>S(2) – Pt(1) – S(1) 104.95(3)</td>
</tr>
<tr>
<td>S(1) – C(1)</td>
<td>1.705(4)</td>
<td>C(1) – S(1) – Pt(1) 85.64(13)</td>
</tr>
<tr>
<td>S(2) – C(1)</td>
<td>1.693(4)</td>
<td>C(1) – S(2) – Pt(1) 86.15(14)</td>
</tr>
<tr>
<td>O(1) – C(1)</td>
<td>1.513(5)</td>
<td>C(1) – O(1) – C(2) 117.3(3)</td>
</tr>
<tr>
<td>O(1) – C(2)</td>
<td>1.469(5)</td>
<td>O(1) – C(2) – C(3) 107.0(3)</td>
</tr>
<tr>
<td>C(2) – C(3)</td>
<td>1.495(6)</td>
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</tr>
</tbody>
</table>

3.4 Deposition of metal chalcogenides thin films from [M(S₂COR)₂], M = Pt, Pd, Ni, Cd and Co; R = Et or Pr

3.4.1 The TGA analysis of [Ni(S₂COR)₂], R = Et or Pr

Thermogravimetric analyses of [Ni(S₂COR)₂] was carried out at atmospheric pressure with N₂ as the carrier gas. The heating rate was 10 °C/min. The TGA curve shown in Figure 3.7, reveals that the precursor decomposed between ca. 155-200 °C with a weight loss of 67 %, leaving 33 % residue which corresponds to theoretical calculated NiS(30%).

Only one stage decomposition was observed on both complexes.
Deposition of Metal sulphide thin films from xanthate precursors

Figure 3.7 TGA curve of [Ni(C₂H₅OCS₂)₂]

The TGA curve of [Ni(C₃H₇OCS₂)₂] in Figure 3.8, showed a massive weight loss between ca. 167-202 °C corresponding to 72 % weight loss (Figure 3.8), leaving 28 % residue which correspond to theoretical calculated NiS.

Figure 3.8 TGA curve of [Ni(C₃H₇OCS₂)₂]
3.4.2 Deposition of NiS thin films from [Ni(S₂COR₂)]₂, R = Et or iPr

TGA analyses showed that the precursors are highly volatile, making them suitable for AACVD and LP-MOCVD studies.

Thin films of NiS were deposited from [Ni(S₂COR₂)]₂, R = Et or iPr at 200 °C, 250 °C, and 300 °C by AACVD. Good quality crystalline films were grown on the substrate at these temperature regions. The films obtained were grey in colour, adherent to the glass substrate. The crystallinity of the prepared NiS samples was investigated by XRD as shown in Figure 3.9-3.14. X-ray diffraction data for NiS reveal that the films prepared by the present methods are polycrystalline in nature and their observed d values are in good agreement with literature value (JCPDS: 12-0041) data file, shown in Table 3.1.

![XRD pattern of NiS from [Ni(C₂H₅OCS₂)]₂ at 200 °C](image)

**Figure 3.9** XRD pattern of NiS from [Ni(C₂H₅OCS₂)]₂ at 200 °C

The observed values suggest that the formed materials is NiS with rhombohedral crystal structure. It is interesting to find out that all the samples can be indexed as
Deposition of Metal sulphide thin films from xanthate precursors

rhombohedral phase NiS with characteristic (110), (101), (300), (021), and (330) planes (Figure 3.9).

The indices are assigned according to those in JCPDS (12-0041). The (300) orientation is dominant but also the other main peaks indicate that the as-grown materials are NiS.

![XRD pattern](image)

**Figure 3.10** XRD pattern of NiS from [Ni(C_2H_5OCS_2)_2] at 250 °C

Growth of NiS from [Ni(C_3H_7OCS_2)_2] at 200 °C (Figure 3.12) differs from those grown from ethylxanthate at a similar temperature. This is due to the instrument noise. This can be seen by NiS deposited at 250 °C (Figure 3.13) which is similar to the NiS deposited from ethyl xanthate precursor at the same temperature.
Deposition of Metal sulphide thin films from xanthate precursors

Figure 3.11 XRD pattern of NiS from [Ni(C₂H₃OCS₂)₂] at 300 °C

Figure 3.12 XRD pattern of NiS from [Ni(C₃H₇OCS₂)₂] at 200 °C
Figure 3.13 XRD pattern of NiS from [Ni(C₃H₇OCS₂)₂] at 250 °C

Figure 3.14 XRD pattern of NiS from [Ni(C₃H₇OCS₂)₂] at 300 °C
Deposition of Metal sulphide thin films from xanthate precursors

Table 3.8 X-ray data of NiS (rhombohedral) thin films from [Ni(S₂COR)₂], R = Et or iPr

<table>
<thead>
<tr>
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<th>d(lit)/Å (% I)</th>
<th>d(exp)/Å (% I)</th>
<th>hkl</th>
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<td>1.82 (17)</td>
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<tr>
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<td>2.94 (26)</td>
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<td>1.63 (18)</td>
<td>1.63 (10)</td>
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<td>1.55 (11)</td>
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<tr>
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<td>1.39 (8)</td>
<td>1.39 (6)</td>
</tr>
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<td>1.33 (4)</td>
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<td>1.30 (5)</td>
</tr>
<tr>
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<td>1.81 (22)</td>
<td>042</td>
<td>1.26 (8)</td>
<td>1.25 (7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>440</td>
<td>1.20 (6)</td>
<td>1.19 (5)</td>
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</table>

Only one phase of NiS has been observed regardless of growth temperature which indicates the thermal stability of the precursors.

The surface morphology of the NiS deposited was studied by SEM. The SEM studies show that the morphology of the films changed with temperature. At 200 °C NiS films with rod-like dimensions were observed (Figure 3.15). These structures were approximately 500 nm in length and 250 nm in breadth, with uniform coverage on the substrate. At 200 °C and 250 °C (Figure 3.16) the films observed could be described as granular nodular in shape similar to those grown at 250 °C from [Ni(C₂H₅OCS₂)₂]. 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 (Figure 3.17), where granular close-to spherical particles are observed. The coverage is non-uniform with clustered growth predominant on the substrate.

Figure 3.15 SEM micrographs of NiS from [Ni(C₂H₅OCS₂)₂] at 200 °C
There is a distinct increase in grain size as the temperature of deposition is increased from 200 to 300 °C (Figure 3.15-3.17). However the films grown at 300 °C are similar to those grown from the ethyl analogue at this temperature. Clustered growth of spherical particles is predominant on the substrate.

**Figure 3.16** SEM micrographs of NiS from [Ni(C₂H₅OCS₂)₂] at 250 °C
Deposition of Metal sulphide thin films from xanthate precursors

Figure 3.17 SEM micrographs of NiS from [Ni(C$_2$H$_5$OCS$_2$)$_2$] at 300 °C

The NiS grown at 200 °C differs from that grown from the ethylxanthate at the same temperature. The particles of the films grown at 200 °C and 250 °C from [Ni(C$_3$H$_7$OCS$_2$)$_2$] are irregular shaped similar to those grown at 250 °C from [Ni(C$_2$H$_5$OCS$_2$)$_2$]. The films grown at 300 °C (Figure 3.18a) are also similar to those grown from the ethyl derivative. The spherical particles form clusters on the substrate.
Figure 3.18 SEM micrographs of NiS from [Ni(C₃H₇OCS₂)₂] at (a) 200 °C, (b) 250 °C, and (c) 300 °C.
EDAX clearly confirms the presence of nickel and sulphur as 1:1 ratio, in all samples. Cheon, et al.\textsuperscript{116} has grown NiS thin films by thermal and photolytic processes. The films grown by the thermal process were found to have relatively rough surface and are highly orientated polycrystalline materials, and while those grown by the photolytic process were smooth and were either non orientated polycrystalline or non diffraction materials. SEM showed that the films consisted of granules. O'Brien, et al.\textsuperscript{56} obtained two different kinds of nickel sulphide (NiS\textsubscript{1.03} and NiS) phases using Ni(SCNRR')\textsubscript{2}, RR' = Et\textsubscript{2}, MeE\textsubscript{t}, Me\textsubscript{t}Bu and Me\textsubscript{t}Hex. Different shapes (wire, tangled wires and platelets) were obtained depending on the growth conditions.

3.4.3 The TGA analysis of [Cd(S\textsubscript{2}COR)\textsubscript{2}], R = Et or \textsuperscript{3}Pr

The TGA analysis of [Cd(C\textsubscript{2}H\textsubscript{5}OCS\subscript{2})\textsubscript{2}] reveals that the precursor decomposed between ca. 160-169 °C with a weight loss of approximately 58 %, leaving 42 % residue which corresponds to the theoretical calculated CdS(40 %).

TGA analysis of [Cd(C\textsubscript{3}H\textsubscript{5}7OCS\subscript{2})\textsubscript{2}] shows that the precursor decomposed between 165-335 °C with a weight loss of 62 %, leaving 38 % which correspond to the theoretical calculated CdS(38 %).

3.4.4 Deposition of CdS thin films from [Cd(S\textsubscript{2}COR)\textsubscript{2}], R = Et or \textsuperscript{3}Pr

Clearly from the TGA analysis both complexes are expected to be suitable for deposition of thin films by AACVD and LP-MOCVD.

Deposition experiments were carried out by AACVD between 200-300 °C. The planes obtained confirm that the formed material is CdS (Figure 3.19-3.24) with
hexagonal crystal structure. The indices are assigned according to the literature JCPDS (41-1049) as indicated in Table 3.9. The (101) orientation is dominant but also the other main peaks indicate that the as-grown materials are CdS. At 300 °C the CdS films are more crystalline as compared to those obtained at 200 and 350 °C.

Figure 3.19 XRD pattern of CdS from [Cd(C2HsOCS2)2] at 200 °C
Deposition of Metal sulphide thin films from xanthate precursors

Figure 3.20 XRD pattern of CdS from [Cd(C₅H₅OCS₂)₂] at 250 °C

Figure 3.21 XRD pattern of CdS from [Cd(C₅H₅OCS₂)₂] at 300 °C
Figure 3.22 XRD pattern of CdS from [Cd(C₇H₇OCS₂)₂] at 200 °C

Figure 3.23 XRD pattern of CdS from [Cd(C₅H₅OCS₂)₂] at 250 °C

The XRD pattern of CdS films from [Cd(C₇H₇OCS₂)₂] at 200 °C (Figure 3.22) and 250 °C (Figure 3.23) are similar to the XRD of CdS from [Cd(C₅H₅OCS₂)₂] at
Deposition of Metal sulphide thin films from xanthate precursors

300 °C (Figure 3.24). The XRD pattern of CdS films from [Cd(C2H5OCS2)2] at 250 °C (Figure 3.23) is similar to the one at 300 °C (Figure 3.24) from [Cd(C3H7OCS2)2]. Both materials show that they are less crystalline as compared to others.

![Figure 3.24 XRD pattern of CdS from [Cd(C3H7OCS2)2] at 300 °C](image)

Table 3.9 X-ray data of CdS (hexagonal) thin films from [Cd(S2CORO)2], R = Et or iPr

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<th>d(lit)/Å (% I)</th>
<th>d(exp)/Å (% I)</th>
<th>hkl</th>
<th>d(lit)/Å (% I)</th>
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<td>2.07 (55)</td>
<td>2.07 (39)</td>
</tr>
<tr>
<td>002</td>
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<td>1.89 (40)</td>
<td>1.90 (30)</td>
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<tr>
<td>101</td>
<td>3.16 (100)</td>
<td>3.17 (85)</td>
<td>201</td>
<td>1.79 (18)</td>
<td>1.74 (26)</td>
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<tr>
<td>102</td>
<td>2.45 (25)</td>
<td>2.40 (10)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
All the CdS films deposited at different temperatures were indexed as the hexagonal phase CdS with the characteristic (100), (002), (101), (102), (110) and (200) planes visible in the XRD patterns.

The morphology of the CdS thin films were investigated by SEM.

Figure 3.25 SEM micrographs of CdS from [Cd(C_2H_5OCS)_2] at 200 °C
Poor coverage of the substrates is observed for deposition at 200 °C (Figure 3.25), and 250 °C (Figure 3.26) with individual spherical shape particles (Shallow circular domes randomly present on the surface).

Figure 3.26 SEM micrographs of CdS from [Cd(C₂H₅OCS₂)₂] at 250 °C

CdS films deposited from [Cd(C₂H₅OCS₂)₂] at 300 °C (Figure 3.27) showed that the morphology of the films has improved. Full coverage of the substrate is observed for
films at 300 °C. SEM images reveal that the films consist of densely packed grains. At higher growth temperature, an increase in particle size was observed. The morphology is similar to the one reported by Hasoon, et al.\textsuperscript{124}

Figure 3.27 SEM micrographs of CdS from $[\text{Cd(C}_2\text{H}_5\text{OCS}_2\text{)}_2]$ at 300 °C
In conclusion, the increase in temperature resulted in markedly different surface morphology, as much finer grains than those observed in Figure 3.25 and 3.26. This shows homogenous nucleation of CdS particles.

SEM of the CdS thin films deposited from $[\text{Cd}(\text{C}_3\text{H}_7\text{OCS}_2)_2]$ at 200 °C (Figure 3.28a) is similar to CdS images at 200 (Figure 3.25) and 250 °C (Figure 3.26) from $[\text{Cd}(\text{C}_2\text{H}_5\text{OCS}_2)_2]$. At 300 °C (Figure 3.28a and 3.28b) uniform materials are observed. This further confirms that temperature plays an important role on the morphology of the films. The morphology of the films is similar to the one previously reported by Hasoon, et al.\textsuperscript{124}

Afzaal, et al.\textsuperscript{120} deposited CdS thin films from $[\text{Cd}\{\text{NSiPr}_2\}_{2}]$. XRD pattern has indicated that only hexagonal CdS films were deposited with the preferred orientation along the (002) plane. SEM studies indicated that the morphology of film consists of randomly orientated domains of compacted thin acicular crystallites with ca. 1.75 μm in thickness. The results seem to indicate that ultrasonication suppresses the growth of CdS grains. There was nucleation of CdS throughout the substrate surface. The film was of denser and more uniform structures.

An EDAX profile of the films confirms the presence of cadmium and sulphur as 1.1 ratios. Similarities in the EDAX profiles between 200-300 °C suggest that the stoichiometry of the films is not affected greatly by the growth temperature.
Figure 3.28 SEM micrographs of CdS from [Cd(C₃H₇OCS₂)₂] at (a) 200 °C, (b) 250 °C, and (c) 300 °C.
3.4.5 The TGA analysis [Pd(S₂COCHR₂)₂], R = Et or iPr

The TGA analysis shows that the first decomposition step is associated with the rapid loss in weight of 44% from [Pd(C₂H₅OCS₂)₂]. This is followed by a much lower decomposition step, in which there is evidence of a two step breakdown. About 58% weight loss of the precursor is observed, leaving 42% residue which correspond to the theoretical calculated PdS(40%).

The TGA curve of [Pd(C₃H₇OCS₂)₂] is similar to that of ethyl palladium complex with the first decomposition step having a weight loss of 46%. About 66% of the precursor decomposes, leaving 37% residue which corresponds to the theoretical calculated PdS(37%).

3.4.6 Deposition of PdS from [Pd(S₂COCHR₂)₂], R = Et or iPr

Deposition of palladium sulphide thin films was carried out by AACVD between 200-300 °C. XRD shows that the Pd₁₆S₇ phase was deposited in this temperature region (Figure 3.29-3.31) with cubic crystal structure. The indices are assigned according to those in JCPDS 11-001. The XRD patterns of the films grown at various growth temperatures show a preferred orientation as the (222) plane regardless of the growth temperatures.
Deposition of Metal sulphide thin films from xanthate precursors

Figure 3.29: XRD pattern of Pd$_{16}$S$_7$ from [Pd(C$_2$H$_5$OCS$_2$)$_2$] at 200 °C

Figure 3.30: XRD pattern of Pd$_{16}$S$_7$ from [Pd(C$_2$H$_5$OCS$_2$)$_2$] at 250 °C
Deposition of Metal sulphide thin films from xanthate precursors

Figure 3.31 XRD pattern of Pd$_{16}$S$_7$ from [Pd(C$_2$H$_5$OCS)$_2$] at 300 °C

Table 3.10 X-ray data of Pd$_{16}$S$_7$ (Cubic) thin films from [Pd(S$_2$COR)$_2$], R = Et or iPr

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<thead>
<tr>
<th>hkl</th>
<th>d(lit)/Å (% I)</th>
<th>d(exp)/Å (% I)</th>
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<td>222</td>
<td>2.58 (60)</td>
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<td>510</td>
<td>1.74 (60)</td>
<td>1.73 (37)</td>
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<td>1.60 (41)</td>
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<tr>
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<td>2.09 (39)</td>
<td>530</td>
<td>1.53 (60)</td>
<td>1.55 (22)</td>
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<tr>
<td>332</td>
<td>1.90 (30)</td>
<td>1.86 (84)</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

The shape of the palladium sulphide films was investigated by SEM. No images were observed at 200 °C, this is due to the amorphous nature of the palladium chalcogenide.
films. The SEM of Pd$_{16}$S$_7$ thin films deposited at 250 °C (Figure 3.32) are dense but uneven on the substrate.

Figure 3.32 SEM micrographs of Pd$_{16}$S$_7$ from [Pd(C$_2$H$_5$OCS)$_2$] at 250 °C
At 300 °C (Figure 3.33) the film is dominated by submicron grains. Gross discontinuities in the PdS films and high density of pinholes were observed. Cheon, et al.\textsuperscript{114} prepared PdS films from [Pd(S\textsubscript{2}COCHMe\textsubscript{2})] and the diffraction of the films showed nonoriented polycrystalline tetragonal PdS. SEM images showed that the films were smooth with shallow circular domes randomly present on the flat surface.
3.4.7 The TGA analysis of \([\text{Pt}(\text{SzCOR})_2], \text{R} = \text{Et or } ^1\text{Pr}\)

The TGA analysis shows that in the initial decomposition there was massive weight loss of 30%. This is followed by a small weight loss, giving 41% mass of the precursor decomposed, leaving about 59% residue which correspond to the theoretical calculated \(\text{PtSz(59\%)}\). The TGA of \([\text{Pt}(\text{C}_3\text{H}_7\text{OCS})_2]\) in is similar to ethyl palladium complex.

3.4.8 Deposition of Pt thin films from \([\text{Pt}(\text{SzCOR})_2], \text{R} = \text{Et or } ^1\text{Pr}\)

Platinum thin films were deposited by AACVD between 200-300°C. Yellow platinum films were observed. XRD patterns show that the films at 200°C (Figure 3.34) and 250°C (Figure 3.35) are not crystalline. Broadened peaks suggest some amorphous nature in the films; the pattern corresponds to that of Pt film.

![XRD pattern of Pt from \([\text{Pt}(\text{C}_2\text{H}_5\text{OCS})_2]\) at 200°C](image)

**Figure 3.34** XRD pattern of Pt from \([\text{Pt}(\text{C}_2\text{H}_5\text{OCS})_2]\) at 200°C
Deposition of Metal sulphide thin films from xanthate precursors

Figure 3.35 XRD pattern of Pt from [Pt(C₂H₅OCS₂)₂] at 250 °C

Figure 3.36 XRD pattern of Pt from [Pt(C₂H₅OCS₂)₂] at 300 °C

The XRD of the platinum at 300 °C (Figure 3.36) from [Pt(C₂H₅OCS₂)₂] reveals that the films are crystalline. From the observed values, the deposited material is indexed...
3.4.10 Deposition of Co₉S₈ thin films from [Co(S₂COR)₂], R = Et or ¹Pr

From the TGA analysis, both precursors are expected to be suitable for AACVD and LP-MOCVD.

Deposition of cobalt sulphide thin films was achieved by AACVD between 200-300 °C. Thin films were found to be reflective and silvery. The films were homogeneous and cover the glass substrate uniformly. The XRD patterns are shown in Figure 3.37-39 which corresponds to Co₉S₈ phase. The films had a predominant (222), (400), (600) with relatively weak intensities when compared with other diffraction peaks.

![XRD pattern of Co₉S₈ films from [Co(C₂H₅OCS₂)₂] at 200 °C](image)

**Figure 3.37** XRD pattern of Co₉S₈ films from [Co(C₂H₅OCS₂)₂] at 200 °C

At higher temperature, the degree of crystallinity of the as-deposited films improved as indicated by XRD (Figure 3.39).
Deposition of Metal sulphide thin films from xanthate precursors

Figure 3.38 XRD pattern of Co$_9$S$_8$ films from [Co(C$_2$H$_5$OCS)$_2$] at 250 °C

Figure 3.39 XRD pattern of Co$_9$S$_8$ from [Co(C$_2$H$_5$OCS)$_2$] at 300 °C

All the films gave very narrow, strong peaks in the XRD patterns. The diffraction patterns observed are summarised in Table 3.12.
Deposition of Metal sulphide thin films from xanthate precursors

Table 3.12 X-ray data of Co₉S₈ (Cubic) thin films from [Co(S₂COR)₂], where R = Et or iPr

<table>
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<th>hkl</th>
<th>d(lit)/Å (% I)</th>
<th>d(exp)/Å (% I)</th>
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<td>511</td>
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The morphology of the films was investigated by SEM. At lower temperature the films are small with shallow circular domes randomly present on the flat surface. At higher temperatures the films are smooth and featureless. The coverage is non-uniform with clustered growth predominant on the substrate. The spherical particles form clusters on the substrate.
Figure 3.40 SEM micrographs of Co₉S₈ from [Co(C₂H₅OCS₂)₂] at 200 °C.

There is, however, a change of morphology at 250 and 300 °C. The coverage is non-uniform with clustered growth predominant on the substrate. EDAX analysis of the as-deposited films shows the presence of cobalt and sulphur.
Figure 3.41 SEM micrographs of Co₉S₈ from [Co(C₂H₅OCS₂)₂] at 250 °C
The TGA analysis of \([\text{Cu(C}_2\text{H}_5\text{OCS}_2\text{)}_2]\)

TGA analysis shows that the precursor decomposed between 77-209 °C with a weight loss of 68 %, leaving 32 % which correspond to the theoretical calculated CuS(32 %).
3.4.12 Deposition of CuS thin films from [Cu(C$_2$H$_5$OCS$_2$)$_2$]

Depositions of thin films were attempted by AACVD between 200-300 °C. Very low solubility of [Cu(C$_2$H$_5$OCS$_2$)$_2$] precursor in tetrahydrofuran or toluene leads to little or no deposition on the glass substrate. No images were obtained due to poor coverage of the materials on the glass substrate. A summary of the colour of the films deposited at different temperature is given in Table 3.13.

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<th>Compound</th>
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<th>Theoretical % residue(nature of residue)</th>
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<td>33</td>
<td>NiS(30 %)</td>
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<td>28</td>
<td>NiS(28 %)</td>
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<td>[Cd(C$_2$H$_5$OCS$_2$)$_2$]</td>
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<td>PdS(40 %)</td>
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Table 3.14 Metal sulfide thin film properties

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</tr>
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</tr>
<tr>
<td>3. Pt(S₂COC₂H₃)₂</td>
<td>Shiny black</td>
</tr>
<tr>
<td>4. Co(S₂COC₂H₃)₂</td>
<td>Shiny black</td>
</tr>
<tr>
<td>5. Cd(S₂COC₂H₃)₂</td>
<td>Yellow</td>
</tr>
<tr>
<td>6. Cu(S₂COC₂H₃)₂</td>
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</tr>
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<td>8. Pd(S₂COCHMe₂)₂</td>
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</tbody>
</table>

3.5 Conclusions

Thin films of metal sulphide were grown from the single-source precursors of the type [M(S₂COCHR₂)₂], M = Ni, Pd, Pt, Cd and Co, and R = ethyl or isopropyl at low temperature under AACVD conditions. In all the samples, the [M(S₂COR)₂, M = Pt, Pd, and Ni , R = Et X-ray structures adopt a square planar geometry. All the metal complexes were characterised by elemental analysis, IR, MS, ¹H NMR and ¹³C. Thin films of NiS, CdS, Pt, PdS, Pd₁₀S₇, and Co₉S₈ were deposited by (AACVD) using the
Deposition of Metal sulphide thin films from xanthate precursors

respective metal xanthate complexes. The structural characteristics of the films were investigated by XRD, SEM, and EDAX. XRD studies show that the NiS is highly orientated rhombohedral phase. All the samples were indexed as rhombohedral NiS with characteristic XRD peaks for (110), (101), (300), (021), and (220) planes. All samples show a strong peak at 32.20° which is assigned to rhombohedral phase (300) diffraction. The NiS thin films are polycrystalline and their features are in good agreement with those reported in literature. The phases do not seem to be affected by temperature whereas the morphology of the films changes with temperature. In contrast the morphology of the films has been found to be greatly influenced by varying the temperature.

The morphology of the films show granular, rod-like and twinned cube shape depending on the temperature of deposition. All the samples of CdS films deposited at different temperature were indexed as the hexagonal phase. Shallow circular domes and grains were obtained by SEM. Broad peaks for Pt films were obtained and the films were indexed as cubic phase. This shows that Pt films are amorphous in nature. Poorly resolved XRD pattern of Co₅S₈ was obtained by XRD. Shallow circular domes were obtained by SEM.

\[M(S₂COCHR₂)₂], M = Ni, Pd, Pt, Cd and Co, and R = ethyl or isopropyl proved to be suitable precursors, with low volatility and stability as well as adequate purity, for the film deposition. This has been demonstrated by one phase deposition.
Chapter 4

Synthesis of CdS Nanoparticles and Nanorods
4.1. General Introduction

There has already been much progress in the synthesis, assembly and fabrication of nanomaterials, and, equally importantly, in the potential applications of these materials in a wide variety of technologies. Preparation, characterization and exploitation of nanosized materials remain the major challenges in the next decade. Nanotechnology has shown potential application in the chemical, energy, electronics and space industries.125-126

Reducing the size of solid materials to nanometric scales leads to a change in their properties. As the size of the solid becomes smaller the band gap gradually becomes larger due to quantum effects. The particle shape, size, and size distribution play important roles in determining its electrical, optical, magnetic and chemical properties.127-128 The control of the size, distribution, and shape of nanocrystals has been a primary focus of research recently.

In this chapter the synthesis of CdS nanoparticles and nanorods from [Cd(S2CNMe2)2] and [Cd{SC(=S)OCH(CH3)2}4] precursors will be described. The synthetic route used is the ‘one-pot’ thermolysis of single-molecule precursors in a high boiling point co-ordinating solvent. The optical properties of the particles were studied using absorption and photoluminescence spectroscopy. The particles were characterized using X-ray diffraction and electron microscopy techniques.

4.2 Optical properties of nanoparticles

Quantum size effects have been observed experimentally for many nanocrystalline semiconductors.129-132 The optical absorption spectrum of a nanocrystalline
Semiconductor provides an accessible and simple method for the evaluation of quantum size effects. The absorption of a photon, leading to excitation of an electron from the valence band to the conduction band of the semiconductor along with a hole in the conduction band, is associated with the band gap energy, $E_g$. The absorption of photons with energy similar to that of the band gap, $h\nu \geq E_g$, leads to an optical transition producing an electron in the conduction band of the semiconductor along with a hole in the valence band. In the absorption process, a photon of discrete energy excites an electron from the valence to the conduction band. This absorption spectrum can be used to determine the energy gap of a semiconductor material.

For crystalline materials the electronic transitions occurring on the absorption of light are subject to certain selection rules. Besides $h\nu \geq E_g$, there is the additional requirement that the wave vector must be conserved.

The absorption ($A$) of light by a semiconductor material with thickness, $I$, can be described by an expression analogous to the Beer's law (eq. 4.1),

$$A = \alpha I$$

\textbf{eq. 4.1}

where $\alpha$ represents the absorption coefficient of the solid and a function of the radiation frequencies.

For crystalline materials the electronic transitions occurring on absorption of light are subject to selection rules as in the molecules. The requirement, besides $h\nu \geq E_g$, is that the wave-vector, $k$, should be conserved:
\[ K_e + K_{\text{photon}} = K'_e \]  
\textbf{eq. 4.2}

where \( K_e \) and \( K'_e \) are the electron wave vectors. \( K_{\text{photon}} \) is small when compared with the wave vectors of the electron before \( (K_e) \) and after excitation \( (K'_e) \), which leads to the conservation rule:

\[ K_e = K'_e \]  
\textbf{eq. 4.3}

Therefore for excitation across the narrowest part of the energy gap to occur, the minimum of the conduction band must have the same vector as the maximum of the valence band. Materials with this type of electronic transition are known as direct band gap semiconductors, e.g. GaAs.

\[ \hbar \omega = E_g \]
\[ \Delta k = 0 \]

\( (a) \) Direct transition

\[ \hbar \omega = E_g \]
\[ \Delta k = 0 \]

\( (b) \) Indirect transition

\textbf{Figure 4.1} Excitation across the band gap by photon absorption: (a) direct process; (b) indirect process.\textsuperscript{131}
Synthesis of CdS Nanoparticles and Nanorods

For other semiconductors the lowest energy electronic transition between the valence band and conduction band is formally forbidden. In these indirect band gap semiconductors, e.g. Si, the transitions require the additional interaction of a photon in order that the conservation rule is maintained.

Semiconductors in which there is conservation of the wave vector for optical transitions are referred to as direct band gap semiconductors (Figure 4.1). An important parameter that determines the efficiency of the process, by which a semiconductor absorbs light photons and generates electron-hole pairs, is known as the absorption coefficient, \( \alpha \). The band structure of the semiconductor determines the characteristics of \( \alpha \), which, for direct band gap, is given by:

\[
\alpha hv = \alpha_0 (hv-E_g)^n
\]

where \( \alpha_0 \) is a constant, \( E_g \) is the energy band gap and \( hv \) is the photon energy.

Equation 4.4 gives useful expression relating the absorption coefficient and the photon energy of a direct transition near the threshold. The probability of an electronic transition occurring is greater for direct electron transitions than indirect transitions. For a direct band gap semiconductor, such as ZnO or GaAs, 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 \( k \). As a result electronic transitions are most likely to occur for this configuration. Hence absorption coefficients for direct band gap semiconductors are large, e.g., 99% of light photons with energies near the band gap of CdTe (\( \sim 1.45 \) eV) are absorbed by a 1 \( \mu m \) thick layer. By comparison similar behavior by crystalline silicon (an indirect band gap semiconductor) requires
20 μm thicknesses. In an indirect band gap semiconductor like silicon, an electron cannot be directly excited to the conduction band with energy $E_g$ and additional energy is required in the form of lattice vibrational energy (phonons). The electron then undergoes a change in momentum and we obtain an indirect transition with energy

$$hν = E_g + E_{\text{phonon}}$$  \hspace{1cm} \text{eq. 4.5}

The optical absorption spectrum of a nanocrystalline semiconductor provides an accessible and straightforward method for the evaluation of quantum size effects. The absorption of a photon, leading to excitation of an electron from the valence band to the conduction band, is associated with the band gap energy ($E_g$). The absorption of photons with energy similar to that of the band gap, $hν \geq E_g$, leads to an optical transition producing an electron in the conduction band of the semiconductor along with a hole in the valence band. Absorption of photons with energy much greater than $E_g$ leads to excitations above the conduction band edge; the electrons can lose the excess energy by radiation-less processes.\textsuperscript{131-133}

4.3 Photoluminescence

The luminescence spectra of these materials show a typical red shift in the emission in respect to the corresponding absorption spectrum. Semiconductor nanoparticles often exhibit narrow close-to-band-edge luminescence with lower energy emissions attributed to trapping states (surface-trapped carriers) and defects.\textsuperscript{134} As the particles size decreases the surface/volume ratio increases thereby increasing the number of surface traps. These surface states or defects, normally associated with semiconductor
nanoparticles, are passivated by tri-n-octylphosphine oxide (TOPO). It is well known that the photoluminescence properties of the nanoparticles are strongly dependent on its surface states, surface passivation and size distribution. Smaller nanoparticles are expected to have an increased emission due to the increase oscillator strength. All luminescence spectra have a substantial Stoke's shifts, previously attributed to the systematic metal vacancies being effective trapping sites.\textsuperscript{135-138} Narrow band (15-20 nm), size-tuneable luminescence, with efficiencies at least of order 10 %, observed at room temperature.

4.4 Synthesis of semiconductor nanoparticles using single-molecule precursors

Several synthetic methods for the preparation of semiconductor nanoparticles have been reported.\textsuperscript{133, 139-147} An ideal synthetic route should produce nanoparticles that are pure, crystalline, reasonably monodispersed and have a surface, which is indecently derivatized. Particles satisfying such criteria may be useful in the fabrication of semiconducting devices. The use of single source molecular precursors has proved to be an efficient route for producing pure high quality, crystalline semiconductor nanocrystallites that are stabilized from the surrounding chemical environment by a capping agent. The fabrication of nanoparticles from single molecule precursors is a one-step process, typically carried out at temperatures in the range 200-300 °C. Trindade and O'Brien, \textit{et al.}\textsuperscript{131} pioneered this route that has been used to synthesize nanoparticles such as \([\text{M} = \text{Zn, Cd}; \text{E} = \text{S, Se}].\)

There is a wide range of advantages for using this method:

- One involatile precursor is involved, purification of which is easier than that of two or more volatile precursors, and hence there is less chance of the
incorporation of impurities into the nanoparticles.

- The route avoids the need for volatile, sometimes toxic and/or pyrophoric precursors.
- Some II-VI and III-V nanoparticles are air sensitive. All precursor synthesis is carried out under anaerobic conditions, with the resulting precursors being air and moisture stable.
- Low temperature deposition routes are possible.
- Although there are theoretical models predicting the optical properties of semiconductor nanoparticles, the properties of nanoparticles obtained by new synthetic routes are sometimes hard to anticipate and may lead to particles with unique and unanticipated, but useful properties.

Figure 4.2 Single-source approach for preparing semiconductor nanocrystallites in TOPO.
Synthesis of CdS Nanoparticles and Nanorods

The synthesis involves the rapid injection of precursor into a hot coordinating solvent (e.g. TOPO) to produce a homogeneous nucleation followed by growth to give surface derivatised nanocrystallites (Figure 4.2).

The use of dithio-/diseleno-carbamato complexes of cadmium/zinc containing asymmetric alkyl groups has proved to be the precursors that give nanoparticles of the highest quality. These precursors are non-air sensitive, stable for a period of months, and easy to prepare and pyrolyse cleanly to give the highest yield. The bis (dialkyldiseleno-carbamato)cadmium(II)/zinc(II) compounds with unsymmetrical R groups like the methyl-hexyl compound, [Cd(Se₂(NMeHex)_2)], produced CdSe nanoparticles of good quality. These observations suggest that the presence of the alkyl groups determine the mechanistic pathway by which the precursor decomposes. Studies on similar compounds, which produce particulate material on thermolysis, have also shown this to be the case. A slight change to the alkyl group drastically alters the deposition mechanistic pathway. Moreover, the mechanism by which a certain precursor decomposes is of fundamental importance to the quality of the resulting nanoparticles. TOPO-capped CdS and CdSe have been synthesized at 250 °C using [Cd(S₂CNMeHex)_2] and [Cd(Se₂CNMeHex)_2] as the precursors. The nanoparticles prepared show a blue shift in the optical spectra in relation to bulk materials. The optical spectra of CdSe shows well-defined excitonic features and the corresponding photoluminescence spectrum was Stoke's shifted in relation to the band edge.
There have been many other types of precursors, all having the metal sulfur bond, that have been used for the synthesis of CdS nanoparticles. The closeness in structure of xanthates in relation to dithiocarbamates makes them ideal precursors for CdS nanoparticles. Cadmium ethylxanthate was thermolysed in TOPO at 160 °C to give monodispersed, spherical TOPO-capped CdS nanoparticles with an average particle size of 4.2 nm. The thermolysis of the identical xanthate precursor in hexadecylamine (HDA) at various temperatures gave rod-shaped CdS nanoparticles. Spherical and non-spherical MS particles (M = Cd, Zn, Pb, Hg, Ni, Cu, Mn) have also been synthesized using metal alkylxanthates in HDA. The authors described the use of reaction time, temperature and/or concentration to achieve size and spectroscopic tunability of the particles. A cadmium(II) complex of dithiobiurea, [Cd(SCNHNH₂)₂Cl₂] has also been used to synthesize CdS nanoparticles with a narrow size distribution. A comparative study of CdS nanoparticles, synthesized under similar conditions in TOPO using bis(methylhexylthiocarbamato)-cadmium(II), cadmium ethylxanthate and a cadmium complex of dithiobiurea, revealed very little differences in the optical and structural properties of the nanoparticles. The narrow PL spectra are characteristic of emission from particles of CdS in the 3-5 nm size regime. The absorption spectra show excitonic features typical of particles in the nanosize regime. The powder X-ray patterns confirms the wurtzite phase in all samples of CdS.

Metal complexes of alkylthioureas have also proven to be very good precursors for nanoparticle synthesis. A series of cadmium(II) complexes with N-alkyl/aryl and N,N'-dialkyl/aryl thioureas (RNHCSNHR'); where R = R' = CH₃, CH₂CH₃, C₆H₅
and/or \( R' = H \) were synthesized by Moloto, et al.\textsuperscript{153-154}. The \([\text{CdCl}_2(\text{CS(NH}_2\text{NHCH}_3)_2]), [\text{CdCl}_2(\text{CS(NH}_2\text{NHCH}_2\text{CH}_3)_2}]\) and \([\text{CdCl}_2(\text{CS(NH}_2)_2])\) complexes were thermolysed in TOPO at 200 °C to give CdS with crystallite sizes of 4.8 nm, 4.3 nm and 32.2 nm from the respective complexes.\textsuperscript{154} There was evidence of agglomeration in all samples from the TEM measurements. Mono- and di-substituted alkylthiourea complexes of lead and copper have been used to prepare PbS and Cu\(_x\)S\(_y\) nanoparticles.\textsuperscript{154} The X-ray diffraction pattern of the PbS confirms a cubic rock-salt phase, with the particles having a predominantly truncated octahedral shape. The copper alkylthiourea complex was added directly into the hot TOPO to give a mixture of nanoparticles suspended in solution and bulk material, which settle at the bottom of the reaction flask. The XRD pattern of the nanoparticles gave a mixture of sulfides of two major stoichiometries, Cu\(_{1.8}\)S (digenite) and Cu\(_{2.1}\)S\(_{1.6}\) (djurleite). The TEM images showed well defined, triangular and hexagonal shaped particles.

4.5 Shape Control of Nanoparticles

One of the recent trends in nanomaterials research is the control of particle shape. The shape of semiconductor nanocrystals does have significant effect on their electronic, magnetic, catalytic and electrical properties.\textsuperscript{155-158} Metal chalcogenides such as CdSe, CdS and PbS remain materials of considerable interest in shape control due to their wide variation in one dimensional morphology with changes in reaction conditions.

For a given solution in the synthesis of nanocrystals one could obtain a variety of shapes, e.g. dots, rods, spindles and tetrapods. As the size of the nanoparticles
Synthesis of CdS Nanoparticles and Nanorods

decreases to their Bohr radius, all the electronic properties begin to change. In this size regime the properties become dependent not only on size but also on their shape. For example if an electron-hole pair (exciton) is formed in a sphere with zero degrees of freedom, the system is known as a “quantum dot”. In this system the exciton is confined in all three dimensions (x, y, z). If the particle is elongated, for example along the c-axis, the exciton formed will still be confined in the x and y direction (a and b) but can be transported along the z, exhibiting the rod-like structure. This suggests that it is confined in two directions but can move along the z-axis. If on the other hand the original sphere (dot) is compressed along the z-axis and equally extended in x and y (e.g. nanodisks), the exciton’s motion is confined in one direction but has room to move along x and y. These are referred to as 2-D structures.

Colvin, et al.\textsuperscript{159} reported the observance of tetrapod and rod-like morphologies of CdSe and CdTe. The influence of temperature, monomer concentration, reaction time and capping group on the particle morphology was also studied by Li et al.\textsuperscript{150}. It was found that the thermolysis of cadmium ethylxanthate in hot hexadecylamine (HDA) gave rod or spherical shape particles depending on the reaction conditions. Moderate temperatures (< 200 °C), high monomer concentration and long reaction times (3 h) gave long multi-armed nanorods. An increase in temperature (260 °C) induced the formation of short single-armed rods. Recently the thermolysis of an N-alkyldithiocarbamato complex of cadmium in HDA gave 1-D CdS nanostructures (single-rods, bent rods or multi-rods) at moderate to high temperatures \textsuperscript{160}. The shape of the nanocrystals varied from longer rods to shorter rods with increased
width by simply increasing the quantity of precursor in the bulk solution from 0.05 g/mL HDA to 1 g/mL HDA at 250 °C.

4.6 General Applications of nanoparticles

Research on nanomaterials has found promising technological applications in many different areas such as microelectronic devices, photo catalysis, electrocatalysis, biomedicine, and chemical processes.\(^{161}\)

4.6.1 Medical and pharmaceutical

Nanomedicine could improve the health and well being of the entire population. Medical technologies provide early detection and diagnosis of diseases or illnesses and enable targeted delivery of pharmaceuticals, nutraceuticals, gene therapy, and sensors; bioengineered tissues to replace damaged or diseased tissues.\(^{162}\)

4.6.2 Drug delivery systems

Shrinking machines down to the size where they can be inserted into the human body in order to detect and repair diseased cells is a popular example for the benefits of nanotechnology. Machine systems will be able to sense and rearrange patterns of molecules in the human body, providing the tools needed to bring about a state of health, regardless of a disease's cause.

Current medical applications of nanotechnology are far more likely to involve improved delivery methods, such as pulmonary or epidermal methods to avoid having to pass through the stomach, encapsulation for both delivery and delayed release, and eventually the integration of detection with delivery, in order for drugs to be delivered.
exactly where they are needed, thus minimizing side effects on healthy tissue and cells. As far as navigation goes, delivery will be by exactly the same method that the human body uses, going with the flow and 'dropping anchor' when the drug encounters its target.  

4.6.3 Health monitoring

Several nano-devices are being developed to keep track of daily changes in patient's physiological variables such as the levels of glucose, of carbon dioxide, and of cholesterol, without the need for drawing blood in a hospital setting. This way, patients suffering from diabetes would know at any given time the concentration of sugar in their blood; similarly, patients with heart diseases would be able to monitor their cholesterol levels constantly. 

Detecting cancerous tumors when they are only a few cells in size. Nanoparticles are targeted to cancer cells for use in the molecular imaging of a malignant lesion. Large numbers of nanoparticles are safely injected into the body and preferentially bind to the cancer cell, defining the anatomical contour of the lesion and making it visible. These nanoparticles give us the ability to see cells and molecules that we otherwise cannot detect through conventional imaging. The ability to pick up what happens in the cell to monitor therapeutic intervention and to see when a cancer cell is mortally wounded or is actually activated is critical to the successful diagnosis and treatment of the disease.
4.6.4 Disease diagnosis and screening

Nanoparticles can be used to pinpoint harmful bacteria in body scans. A new nanoparticle test for dangerous bacteria such as Escherichia coli was found to be more sensitive in such a way that it could detect a single bacterial cell within minutes.

An injection of magnetic nanoparticles into bloodstream could reveal precisely where harmful viruses are lurking. The particles are coated with antibodies to a particular virus, so they will form clumps that should be visible on conventional body scans if that virus is present. 165

4.6.5 Food processing and storage

Waiting a day or two (Test and Hold) for results in food industry can be costly and inconvenient. This can be obviously expensive for industry having large quantity of stock. The nanoparticles are added to a solution of the test sample, such as ground beef. If the bacterium sought is present the nanoparticles will quickly attach to it. The sample is then separated by weight in a centrifuge. The target bacteria, being heavier than the nanoparticles, will separate away from them. But those dye molecules already attached will fluoresce in this heavier sample, identifying the bacteria. 166

4.6.6 Energy storage, production and conversion

Semiconductor nanoparticles have shown great promise in the photonics applications, such as solar cells and light emitting devices, because the wavelength response of the device can be tuned by simply varying the size of the quantum dot. 167 Nanoparticles are used in solar energy conversion. Today's solar panels are made with silicon. The
silicon usually has impurities, which limits its efficiency. Purifying a chemical is too expensive. For that reason, smaller is better.

4.6.7 Construction

Nanomaterials make asphalt and concrete more resistant to water; materials to block ultraviolet and infrared radiation; materials for cheaper and durable housing, surfaces, coatings, glues, concrete, and heat and light exclusion; and self-cleaning for windows, mirrors and toilets. 168

4.6.8 Electronic, Optical and Magnetic applications

Nanomaterials exhibit a great potential applicability in electronic systems. The wide band gap II/VI semiconductors are of current interest for optoelectronic applications such as blue lasers, light emitting diodes, and optical devices based on nonlinear properties. Group II and VI quantum dots will be used in future photonic applications such as solar cells and light emitting diodes, because the wavelength responses of the devices can be tuned by simply varying the size of the quantum dots. Cadmium chalcogenides are also useful material in solid-state photoconductors, field effect transistors, sensors, and transducer. The properties of the nanoparticles change as the size changes and of those properties is the part of the light spectrum it absorbs. ZnSe and ZnS materials are used in blue/blue-green lasers. Zinc sulphide has been used widely in the fields of displays, sensors and lasers. 148 Cadmium selenide fluorescing particles are used in biological labels alongside, or even replacing, fluorescing molecular probes. 149, 169
4.6.9 Data storage

Group 15 chalcogenides are used in a range of applications e.g. semiconductors, optical data storage media, electro-active materials, thermoelectric coolers and photodiode arrays. Miniaturised data storage systems with the necessary long-term stability and capacity comparable to the stock of national libraries, PCs with the power of today’s computer centres, minidisks, which contain e.g. all classical music records, minichips, which contain e.g. all classical music records and optimised reaction chains, and light weight plastic windows with hard transparent protective layers or bearings without lubricant for the automobile industry.170

4.6.10 Catalysis

These materials have possible future applications as photo catalysts in photoreactions. Nanocrystalline TiO2 finds widespread applications in photo catalysis, solar energy conversions, ductile ceramics, sensors and mesoporous membranes.171

4.6.11 Agriculture

Nanotechnological materials are in development for the slow release and efficient dosage of fertilizers for plants and of nutrients and medicines for livestock. Other agricultural developments include nano-sensors to monitor the health of crops and farm animals and magnetic nano-particles to remove soil contaminants.164
4.7 Experimental

4.7.1 Materials

All chemicals used were of analytical grade quality and were used without further purification. Deionized water was used for all experimental work. Tetramethyl thiuram disulfide (97 %, Aldrich), 2,5 dimercapto-1,3,4 thiadiazole (98 %, Aldrich), isopropyl xanthic disulfide (95 %, Aldrich), methanol; toluene; hexadecylamine (HDA, 90 %, Aldrich); tri-n-octylphosphine oxide (TOPO, 90 % Aldrich), tri-n-octylphosphine (TOP, 99 %, Aldrich); potassium tetrachloroplatinate(II); potassium tetrachloropalladate(II); cadmium chloride; and cobalt hexahydrate; cobalt(II) chloride (98 %, Fluka Chemika); copper(II) nitrate hydrate (95 %, BDH); cadmium chloride anhydrous; cadmium chloride (99 %, Aldrich).

4.7.2 Synthesis of Precursors

4.7.2.1 Synthesis of [Cd(S2CNMe2)2]

[Cd(S2CNMe2)2] was prepared by refluxing \{(CH3)2NCS\}2 (1 g, 4.16 mmol) and CdCl2.H2O (0.837 g, 4.16 mmol) in deionised water for 3 h. The resulting precipitate was vacuum filtered. The product was washed several times with water followed by methanol and dried at room temperature. The resulting product is slightly soluble in various solvent. The product can be obtained in high purity without further purification. Yield: 0.105 g, 72 %. MP = 367 °C. C6H12N2S4Cd: Mol. Mass, 353.44; Anal. Calcd: C, 20.45; H, 3.41; N, 7.90. Found: C, 20.35; H, 3.54; N, 7.88. FT-IR (KBr disc): ν (C-N) 1219(s); δ (C-S) 941(m). MS: m/z = 352 correspond to [M + H]+.
4.7.2.2 Synthesis of $[\text{Cd}\{-\text{SC}(=\text{S})\text{OCH}(\text{CH}_3)\}_4]$ 

$[\text{Cd}\{-\text{SC}(=\text{S})\text{OCH}(\text{CH}_3)\}_4]$ was synthesized by dissolving $[\text{SC}(=\text{S})\text{OCH}(\text{CH}_3)]_2$ (1 g, 3.6 mmol) and $\text{Cd}(\text{CH}_3\text{COO})_2$ (0.74 g, 3.7 mmol) in ethanol and refluxing the mixture for 24 h. The precipitate was washed (3 x 10 mL) with methanol. The resulting precipitate was vacuum filtered and dried at room temperature. Yield: 1.68 g, 72 %. MP = 70 °C. $\text{C}_{16}\text{H}_{25}\text{O}_4\text{S}_3\text{Cd}$: Mol. Mass, 652; Anal. Calcd: C, 29.40; H, 4.29; S, 39.26. Found: C, 29.66; H, 4.68; S, 36.78.

4.7.3 Preparation of nanoparticles

4.7.3.1 Synthesis of CdS Nanoparticles from $[\text{Cd}(\text{S}_2\text{CNMe}_2)_2]$ in Tri-n-octylphosphine oxide (TOPO)

$[\text{Cd}(\text{S}_2\text{CNMe}_2)_2]$ (0.5 g, 1.42 mmol) was dispersed in TOP (10 mL) and then injected into hot TOPO (30 g, 78 mmol) at 250 °C. A decrease in temperature of 20-30 °C was observed. The reaction was allowed to continue for 45 min. The solution was allowed to stabilize at 250 °C. A sample was syringed after 5, 10, 20, 30 and 45 min for UV analysis. After completion of the reaction, methanol was added to the cooled mixture (70 °C), to flocculate the nanoparticles. The solid was separated by centrifugation, washed three times with methanol. The resulting yellow solid precipitate, TOPO capped CdS nanoparticles, were dispersed in toluene. The solution was centrifuged and the resulting precipitate was dissolved in toluene.
4.7.3.2 Synthesis of CdS nanoparticles from [Cd(S₂CNMe₂)₂] in hexadecylamine (HDA)

HDA (6.25 g, 25 mmol) was loaded into a reaction flask and then heated to 240 °C under a nitrogen flow. [Cd(S₂CNMe₂)₂] (0.5 g, 1.42 mmol) was dispersed in 5 mL TOP and the solution was rapidly injected into a hot solution of HDA (240 °C). After mixing the solution turns yellow rapidly. Heating was continued to recover the temperature and the reaction was maintained for a 30 min. The solution was cooled gradually under ambient condition to a ca. 70 °C and an excess of methanol was added. The flocculant precipitate formed was centrifuged and the upper-layer was decanted, then the isolated solid was dispersed in toluene. The above centrifugation and isolation procedure was then repeated three times for the purification of the prepared CdS nanocrystals.

4.7.3.3 Synthesis of CdS nanoparticles from [Cd{-SC(=S)OCH(CH₃)₂}₄] in HDA

[Cd{-SC(=S)OCH(CH₃)₂}₄] (0.5 g, 0.77 mmol) was dissolved in TOP (10 mL) and injected into hot HDA (30 g, 78 mmol) at 200 °C. The reaction was allowed to continue for 45 min. A decrease in temperature of 20-30 °C was observed. The solution was allowed to stabilize at 200 °C. After completion of the reaction, methanol was added to the cooled mixture (70 °C), to flocculate the nanoparticles. The solid was separated by centrifugation, washed three times with methanol. The resulting yellow solid precipitate, HDA capped CdS nanoparticles were dispersed in toluene. The solution was centrifuged and the resulting precipitate was dissolved in toluene.
4.8 Results and discussion

4.8.1 Synthesis of CdS nanoparticles from \([\text{Cd}(\text{S}_2\text{CNMe}_2)_2]\) in TOPO

The TGA curve shows that the complex decomposed between 302-370 °C (Figure 4.3) with a weight loss of 68 %.

![TGA curve of \([\text{Cd}(\text{S}_2\text{CNMe}_2)_2]\)](image)

Figure 4.3 TGA curve of \([\text{Cd}(\text{S}_2\text{CNMe}_2)_2]\)

4.8.1.1 Optical and structural properties

The onset of absorption in the UV spectrum of semiconductor nanoparticles is attributed to the band gap absorption. The band gap of particles in the nanometer size regime is blue shifted (shift to shorter wavelengths) relative to the bulk materials counterpart because of quantum confinement. The particle growth was monitored by measuring the optical absorption spectrum of samples withdrawn at various time intervals from the reaction vessel. The spectra of all CdS samples isolated at various
time intervals give features of an ideal sample having particles of narrow size and uniform size distribution.

![Graph showing optical absorption spectra of CdS nanoparticles](image.png)

**Figure 4.4** Optical absorption spectra of CdS nanoparticles

The band gaps of all the samples (5-45 min) show blue shift in relation to bulk CdS (515 nm, Figure 4.4). The absorption edges for the samples are as follows: 5 min (468 nm, 2.60 eV); 10 min (473 nm, 2.57 eV); 20 min (486 nm, 2.51 eV); 30 min (495 nm, 2.46 eV) and 45 min (500 nm, 2.44 eV). The shift in the band edge to the red is observed with increase in time from 5 min to 45 min, an indication of the increase in particle size. An excitonic peak is seen at ca. 460 nm typical of CdS. The increase in particle size with time is consistent with an Ostwald ripening process. \(^{172}\)

The photoluminescence spectra of all samples (5-45 min) were very poor. The emission peaks were broad in the 500-700 nm regions. The emission is probably due to recombination from surface defects (predominantly sulfur vacancies).
4.8.1.1 Structural Characteristics

X-ray diffraction spectroscopy is used to study the crystallinity of the nanoparticles. Typically the XRD pattern has broad peaks, an indication of the nanometric size of the particles. The XRD pattern shows that the CdS nanoparticles are crystalline with a predominantly hexagonal phase (Figure 4.5).

![XRD Pattern](image)

**Figure 4.5** XRD pattern of TOPO capped CdS nanoparticles from [Cd(S₂CNMe₂)₂]

The CdS (110), (103), and (112) planes of wurtzite CdS are clearly distinguishable shown in Figure 4.5.
Table 4.1 X-Ray data of CdS (hexagonal) nanoparticles from [Cd(S₂CNMe₂)₂]

<table>
<thead>
<tr>
<th>hkl</th>
<th>d(lit)/Å (% I)</th>
<th>d(exp)/Å (% I)</th>
<th>hkl</th>
<th>d(lit)/Å (% I)</th>
<th>d(exp)/Å (% I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>3.58 (75)</td>
<td>3.56 (65)</td>
<td>110</td>
<td>2.07 (55)</td>
<td>2.06 (48)</td>
</tr>
<tr>
<td>002</td>
<td>3.37 (60)</td>
<td>3.36 (86)</td>
<td>103</td>
<td>1.89 (40)</td>
<td>1.89 (35)</td>
</tr>
<tr>
<td>101</td>
<td>3.16 (100)</td>
<td>3.16 (83)</td>
<td>112</td>
<td>1.76 (45)</td>
<td>1.75 (41)</td>
</tr>
<tr>
<td>102</td>
<td>2.45 (25)</td>
<td>2.42 (20)</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

The morphology of the as prepared CdS sample was investigated by transmission electron microscopy (TEM). The TEM image (Figure 4.6) shows monodisperse, close to spherical TOPO-capped CdS particles. There is evidence of some agglomeration of the particles in the TOPO matrix. The particle size is in ca. 3-5 nm size range. The determination of the size distribution is difficult as a result of the aggregation.
4.8.2 Synthesis of CdS nanoparticles from [Cd(S₂CNMe₂)₂] in HDA

A similar procedure for the preparation from the precursor was used as described in 4.3.1. TOPO was replaced by HDA as a solvent.
4.8.2.1 Optical and structural properties

The shape of the band edge of the HDA capped CdS sample is similar to that of the TOPO capped sample. The band edge is observed at 480 nm, a blue shift of 35 nm in relation to the bulk material (Figure 4.7). The blue shift is indicative of size quantization.

![Absorption Spectrum](image)

**Figure 4.7** Optical absorption spectra of HDA capped CdS nanoparticles

The photoluminescence spectrum of CdS is red shifted in relation to the corresponding absorption spectra, exhibiting an emission maximum at 520 nm ($\lambda_{\text{exc.}} = 480$ nm) in Figure 4.8. This stokes shifted band edge luminescence has been attributed to emission from a "dark exciton". The broad emission is due to the broad size...
distribution of the particles. There is some evidence of emission trap from trap states in the 480-530 nm region.

![Figure 4.8 PL spectra of HDA capped CdS nanoparticles](image)

**Figure 4.8 PL spectra of HDA capped CdS nanoparticles**

### 4.8.2.2 Structural Characteristics

The XRD pattern of the particles can be indexed to hexagonal CdS with strong (110), (103), and (112) reflections in Figure 4.9. The peaks are sharper than those observed for spherical CdS nanoparticles in TOPO in Figure 4.5.
The TEM micrographs (Figure 4.10) of the HDA capped CdS shows particles that are in the shape of rods. This is in contrast to the TOPO capped particles which are spherical. The particles have an average length 40 nm and breadth of 16 nm. The particles are close to monodisperse with an aspect ratio of ±3. There are many two and three arm rod shaped structures with some tetrapods also observed. The sharper XRD peaks are also evidence of larger (or rod shaped) particles. The observance of rod shaped particles in HDA was also reported by Li, *et al.*,\textsuperscript{150} used cadmium xanthate as a precursor.
HDA absorbs selectively with its amine on the surface of the CdS favoring the formation of anisotropic or elongated morphology and appreciable mobility as compared with TOPO.\textsuperscript{150} TOPO is known to bind very strongly to the surface of the crystal preventing elongated growth, therefore there are no reports of rod shaped particles in TOPO. The tetrapod structures are formed when the wurtzite rods (or arms) form out of the (111) faces of the original zinc blende nucleus.
4.8.3 Preparation of CdS nanoparticles from [Cd{SC(=S)OCH(CH₃)}₄] in HDA

The TGA for the [Cd{SC(=S)OCH(CH₃)}₄] complex shows a multistep decomposition (Figure 4.11).

![TGA curve of [Cd{SC(=S)OCH(CH₃)}₄]](image)

**Figure 4.11** TGA curve of [Cd{SC(=S)OCH(CH₃)}₄]

4.8.3.1 Optical and structural properties

The absorption spectrum exhibits an excitonic shoulder at ca. 330 nm with the band edge observed at 510 nm giving a weak emission peak (Figure 4.12).
4.8.3.2 Structural Characteristics

The XRD pattern shows the presence of the characteristic (002), (110), and (112) planes indexed to the hexagonal phase of CdS (Figure 4.13). The narrow peaks at (100), (002) and (101) show that these nanocrystals are elongated towards the c-axis. The sharpness and strength of the diffraction peaks suggests that the particles are crystalline.
The TEM images show particles that are rod shaped. The rods are slightly shorter than those obtained using the [Cd(S2CNMe2)2] precursor in Figure 4.9. The average length is 18 nm and average breadth is 10 nm (Figure 4.14). There appears to be spherical particles on the TEM grid, however this shape is probably due to particles lying ‘upside down’ on the grid. The rods are similar to the one reported by Christian et al. The rod-like morphology were predominant with rod diameters of 7 nm, and aspect ratios of ±3.
Figure 4.14 TEM images of HDA capped CdS nanorods from
\[ \text{Cd}\{\text{-SC}(=\text{S})\text{OCH(CH}_3\text{)}_2\}_4 \]
4.9 Conclusions

[Cd(S₂CNMe₂)₂] and [Cd{-SC(= S)OCH(CH₃)₂}₄] were used as single molecule precursors for the preparation of nanoparticles and nanorods in HDA and TOPO. It was difficult to recrystallize the cadmium complexes due to their low solubility. The optical absorption spectra show blue shift in the band gap of the CdS nanoparticles. The photoluminescence obtained shows very poor results. The hexagonal phase of CdS was observed for all the CdS samples using powder X-ray diffraction. The TEM images reveal that the TOPO capped CdS nanoparticles have a spherical shape whereas the HDA capped particles were rod shaped.
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178


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