Investigation and characterisation of growth phases of polycrystalline cadmium sulfide thin films produced by the chemical bath deposition method

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Investigation and characterisation of growth phases of polycrystalline Cadmium Sulfide thin films produced by the Chemical Bath Deposition method

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USE OF THESIS

The Use of Thesis statement is not included in this version of the thesis.
Abstract

This research project investigates the characterisation and morphology of the growth phases of polycrystalline CdS thin films that were created using the Chemical Bath Deposition (CBD) method. One batch of CdS thin films was created by the author (group B) whilst another batch (group A) was obtained from a previous research project.

In both cases, the experiments were designed such that successive slides in a set represent successive phases in the growth of these CdS thin films. Therefore analysis of the near surface for all slides in a set gave an accurate representation of conditions on the surface at the corresponding time when each slide was withdrawn from the deposition bowl.

These two sets of CdS thin films were then submitted to analysis using the investigative techniques of PIXE, RBS, AFM, XRD, and ESCA and notable differences were looked for. The XRD and AFM analysis was completed by the author, whilst the PIXE and RBS analysis was accomplished in conjunction with each facility manager. The ESCA analysis was achieved by the facility manager after consultation with the author.

An analysis of the experimental equipment design was also carried out, resulting in a new experimental design, that was built and tested. The results of the analysis highlighted a significant difference between group A and group B CdS thin films. Group A films were hard and adherent to the substrate, appearing homogeneous with good coverage and having smaller, more numerous spherical grains. However, group B films displayed an initial sulphur layer deposited on the substrate with a thicker CdS layer on top which resulted in the films being soft, powdery and not very adherent to the substrate. With group B, the CdS grains were much larger, having much rougher, non-uniform shapes indicating that the particulate phase was dominant during its formation.
Declaration

I certify that this thesis does not, to the best of my knowledge and belief:

(I) incorporate without acknowledgment any material previously submitted for a degree or diploma in any institution of higher education;

(II) contain any material previously published or written by another person except where due reference is made in the text; or

(III) contain any defamatory material.

Signature

Date ..........................21th December, 2001
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And mostly, to my wife and three kids, who put with my usual reply "Not now but later when my thesis is finished!"
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Chapter 1  Introduction

The excellent semiconductor properties of polycrystalline $CdS$ thin films result in its high usage in thin film solar cell research as well as in infrared photodetection and other electronic devices (photoconductors). Polycrystalline $CdS$ is a binary II-VI semiconductor and is being used increasingly in high efficiency, thin film, heterojunction solar cell devices (Tsuji, et al., 2000; Markvart, 1994) as an $n$-type window layer. Some examples are $n$-$CdS$/p-$CdTe$ solar cells (Jayakrishnan, et al., 1996), $n$-$CdS$/p-$InP$ solar cells (Saito, Hashimoto & Ito, 1994) and $n$-$CdS$/p-$InSe_2$ solar cells (Das & Morris, 1993). Also, polycrystalline $CdS$ is used in $HgCdTe$ infrared photodetection imaging devices as a passivator layer (Nemirovsky, 1990). $CdS$ has a significantly large energy band gap of 2.46 eV which allows more than 80% of the useable electromagnetic energy to pass through without being absorbed. When using $CdS$ films in solar cells, only a small fraction of this absorbable electromagnetic energy is actually captured (typically less than 4%) simply because of the films thinness, leaving the bulk of the energy to penetrate into the more efficient $p$-type absorber layers of the solar cell, such as $CdTe$ or $CuInSe_2$.

Chemical Bath Deposition (CBD) is one technique for creating these polycrystalline $CdS$ thin films of thickness typically less than 100 nm and is a relatively simple, low temperature, chemical solution growth process (Giuszak, 1996). The CBD method shows good potential for manufacturing these $CdS$ thin films at a substantially lower cost when compared with other current methods, such as metallorganic chemical vapour deposition (MOCVD) (Streetman, 1995, p.22) or molecular beam epitaxy (MBE) (Streetman, 1995, p.23). Also, the CBD method has the potential to significantly lower the cost of the silicon wafer solar cell by helping to replace the high cost silicon wafer with heterojunction semiconductors that can be far more cheaper to produce.
It is the authors belief that low cost, light weight, high efficiency solar cell arrays on top of home dwellings should be connected into a national grid, where credit is given for electrical generation during the days to offset costs for energy usage during the nights or high demand periods. CdS semiconductors and its associated absorbers, coupled with the CBD process, show the potential to achieve this ideal through the potential production of these low cost, light weight, and high efficiency solar cells.

1.1 Background

The breakthroughs in production techniques of pure, single crystal silicon in the early and mid-1950's has allowed electronic solid state device technology to progress very quickly. Numerous types of semiconductor devices built on substrates of device grade silicon are currently in use, including integrated circuits, central processor units, rectifiers, transistors and silicon solar cells. The main advantages of using silicon are the abundance and cheapness of its raw material; its excellent silicon oxide insulating properties; and performance under lithography. Its disadvantages are silicon is an indirect semiconductor and is subsequently a poor absorber of electromagnetic radiation; pure crystalline silicon is a fundamental requirement for all electronic devices and this silicon has a huge infrastructure cost associated with its manufacture.

The high cost of silicon solar cells dramatically highlights the expense of the silicon manufacturing process. A number of these manufacturing techniques are the horizontal Bridgman method, the Czochrulski method, the liquid-encapsulated Czochralski method, Zone Refining and Floating-Zone Growth methods (Streetman, 1995, p.15). The excessive cost of manufacture and other problems associated with the use of silicon has resulted in other methods and materials being sought as suitable replacements. The current newer methods are really different approaches to what is broadly described as the Epitaxial growth method.
Epitaxy is the process of growing an orientated single crystal or polycrystalline layer on top of a suitable substrate that may be of similar material or another entirely different material. This epitaxy process can be performed at low temperatures and it is possible to grow a variety of crystals for device applications. Epitaxial growth methods have now become the most important and versatile of the crystal growth processes. Many different methods are currently in use for growing these epitaxial films. Some of these methods include metal organic chemical vapour deposition (MOCVD), growth from a melt (liquid phase epitaxy – LPE) (Streetman, 1995, p.19), evaporation of the elements in a vacuum (molecular beam epitaxy – MBE), spray pyrolysis (Lo Savio & Oliveri, 1989), electrodeposition (Chopra & Das, 1983) and chemical bath deposition (CBD) (Dhere, et al., 1995).

The CBD CdS is particularly successful in photo-voltaic cells due to the methods ability to produce very thin adherent polycrystalline layers with excellent surface coverage. The undesirable high resistance aspect of these CdS films is largely negated by the thinness of the films. Also, this resistance of the film decreases under visible light illumination due to the creation of extra charge carriers within the CdS material. Technically, CBD is relatively simple and under the right conditions, dissolved precursors of $Cd^{2+}$ and $S^{2-}$ at very low concentrations will deposit onto any available material surface in preference to precipitating out in the solution. This deposition of the precursors tends to form thin, stable, polycrystalline CdS films, having abrupt junctions with good adhesion to the substrate. The resulting CdS thin film, with its inherent physical properties, are dependent on the initial deposition technique and associated process parameters.

1.2 Significance of Study

A great deal of research has been conducted on CBD methods and the polycrystalline CdS thin films it can produce. Film growth rates have previously been determined and
modelled. Deposited film properties have been found to be strongly dependent on
temperature, relative concentrations of precursors, solutions pH and stirring (Giuszak &
Hinckley, 2001). Morphology and structure investigations have and are been conducted
with different analytical methods to determine how, with the CBD method, the CdS is
bonding to the surface of the substrate and how this CdS builds up to form a polycrystalline
thin film during the deposition process.

This project will investigate the process of nucleation and the growth of atomic
structures within the CdS film created via the CBD technique. The structure of the CdS
film is very important as it determines the films properties and suitability in photo devices.

1.3 Research Questions

The quality and properties of these polycrystalline CdS thin films is determined by the
process that creates them. Thorough understanding of this CdS thin film formation process
is then critical if precise control of the process is to be achieved. Aspects of the CdS thin
film formation process that need to be investigated are:

- What type of growth mechanism on the surface of the substrate, is occurring?
- What type of unit cell structures can be found in the CdS thin film?
- What are the preferred orientations of these possible unit cell structures?
- How many times does the unit cell repeat itself (what is the average grain size)?
- Is the Cd to S atomic ratio 1 to 1?
- Is this Cd to S atomic ratio consistent throughout the bulk of the thin film?
- What other elements are found in the film besides Cd and S?
- Are other compounds forming besides CdS?
1.4 Limitations

As Edith Cowan University has no surface material analytical equipment, therefore use of facilities sited at other universities and organisations was required.

There is also the consideration of time constraints. The original batches of polycrystalline CdS thin films were created in 1996 via a particular CBD technique and required approximately three months of experimentation to get to a stage where the thin films produced were of consistent, high quality. The latter experiments (group B) had approximately one month to try and achieve the same quality before scheduled testing began.

Access to other universities facilities was a problem for only one type of experiment. The required analysis was started three months behind schedule and was due to a priority experiment requiring a series of week-long analysis runs. When access was finally gained there were continuing problems with equipment setups, aborted runs, unscheduled maintenance, scheduled maintenance and other students wanting to use the analysis machine. Results were finally achieved only after another three months from the start date of the actual analysis.

With each analysis machine comes associated software such as RUMP software for RBS (Thompson, 1998) and MDI Jade 5.0 for XRD (Materials Data Inc.). These software packages are very powerful tools but also require a fair amount of usage before they can be manipulated effectively. RUMP is a text based program and it caused considerable frustration simply because it is not user friendly. The time required to achieve the needed proficiency to use these software packages, proved to be a problem.
1.5 Objectives

The main aims of this project are

- To create a number of batches of thin film, polycrystalline Cadmium Sulfide (CdS) slides in the laboratory using apparatus and techniques previously formulated.

- To analyse the structure, composition and optical properties of experimentally produced polycrystalline CdS thin films, during successive stages of deposition, by using many different analytical techniques.

- To determine growth phases and structures at successive stages during film formation.

- To compare these newly created polycrystalline CdS thin films (group B) with other polycrystalline CdS thin films obtained from previous CBD experiments (group A).

- To review the experimental apparatus setup used for creation of these polycrystalline CdS thin films with the view of improving / enhancing the experiment.

- To gain good practical experience and efficiency on the use of varied analytical techniques (PIXE, RBS, AFM, XRD, and ESCA), associated equipment and analytical software packages.
Chapter 2 Literature Review

The first report of Chemical Bath Deposition (CBD) was in 1884 by J.E. Reynolds (Journal of Chemical Society, 45, 1884, 162) for the deposition of Lead Sulphide (PbS). But it wasn’t until the early 1960’s and into the 1970’s that considerable interest was generated by the solution growth technique for creating semiconductor thin films, which offered an attractive possible alternative to the then commonly used methods of vacuum evaporation, sputtering and spray pyrolysis. The CBD method was seen to be inexpensive and a convenient method for large area preparation of thin films at low temperature. Because it is a low temperature deposition method (less than 90°C), CBD does not limit the choice of substrate material. By contrast, spray pyrolysis is limited to using only a small number of substrate materials that can withstand the high temperatures and chemical corrosion during deposition. Also, the vacuum evaporation deposition technique requires a critical adjustment of the substrate and various source temperatures, as well as the adjustment of the concentrations of the various components, for the formation of homogeneous and stoichiometric compound films.

Much of the CBD experimentation during these years was mainly recipe orientated, the experiments were aimed at using different solutions for creation of varied type compound semiconductor thin films (eg CdS, PbS, PbSe, CdSe and ZnSe) on different substrates (Kaur, Pandya & Chopra, 1980). Early analysis of these CBD thin films was by photoconductance, spectral response, dark conductivity and UV/VIS which relate to the semiconductors electrical / electronic properties. Towards the late 1970’s and onwards, the kinetics and mechanism of growth of these thin films via CBD were studied, especially in relation to the CdS semiconductor, as its importance in alternative solar cell fabrication had become significant (Uda, et al., 1978). The effects of temperature, solution pH, solution
concentrations, chemical reactions, types of compounds used were examined and models formulated to try and explain the mechanisms involved in the creation of the \textit{CdS} thin film. Additional analysis techniques such as XRD, SIMS, ESCA, SEM, RBS etc., were also being used to investigate the \textit{CdS} structures forming at the substrate surface via the CBD process. The newer analysis techniques revealed information such as \textit{CdS}'s preferred growth structures for the CBD method, orientations of crystal structures, size of nucleation sites, identification of dominant and trace compounds at the surface of the \textit{CdS} thin film, etc. Analysis of these \textit{CdS} thin films from various experimental groups supported similar findings as well as adding to the bulk of knowledge.

XRD analysis by various researchers (Bhushan & Sharma, 1992; Gluszak, 1996; Kaur, Pandya & Chopra, 1980) have shown that under optimal conditions the \textit{CdS} tend to form cubic and hexagonal polycrystalline structures, though other research has shown that by modifying the environment (initial conditions as well as continuing conditions), either the hexagonal phase or the cubic phase can dominate these films. For example, the use of vigorous stirring during CBD has been shown (Kaur, et al., 1980) to result in hexagonal phase polycrystalline \textit{CdS} thin films (type A) that are adherent, physically coherent and specularly reflecting. Alternatively, using specific initial concentrations of ammonia solution with respect to the cadmium salt, resulted in the cubic phase becoming dominant, with or without stirring (Kaur, et al.) These cubic structure polycrystalline \textit{CdS} thin films (type B) tend to exhibit inferior qualities, being less reflecting, powdery and less adherent to the substrate surface. Further, XRD revealed that annealing the polycrystalline \textit{CdS} thin films in air (Nair, Nair, Zingaro & Meyers, 1993; Sebastian & Hu, 1994; Gluszak & Hinckley, 1998) at temperatures above 400\textdegree C for periods of hours resulted in the transformation of these cubic structures into hexagonal structures, this hexagonal phase remaining when the films cooled. At the same time, XRD has also shown that these cubic
structures remain if the annealing process takes place in different atmospheres other than air (Melo, et al., 1994)

ESCA analysis has shown that many elements can be found on the surface of \textit{CdS} thin films made with the CBD method. These naturally include cadmium and sulphur as well oxygen and carbon. The carbon is evident in all ESCA data, being found only on the very surface, and is easily removed by sputtering off the very top layer of the film. This carbon is usually a product of contamination after the experiment ie handling of or breathing on the film. Compounds are also found and these include sulphates, hydroxides, dioxides and oxides as reported by different researchers (Danaher, Lyons & Morris, 1985; Niles, Herd & Al-Jassim, 1997; Jayakrishnan, et al., 1996; Rieke & Bentjen, 1992).

Imaging techniques such as SEM and AFM supply visual data that allow researchers to see fault formation, nucleation sites, roughness, grain sizes and shapes, layers, coverage, projections and lattice mismatch. Morphological analysis of the surface of \textit{CdS} thin films show that type A films display characteristic homogeneous, small grain, fairly spherical structures with good coverage (Gluszak, 1996) whilst type B films display varying heterogenous structures with much larger and fewer grains, having much rougher, non-uniform shapes (Dhere, et al., 1995; Tsuji, et al., 2000).

2.1 General Overview of Findings

Analysis and characterisation of CBD \textit{CdS} thin films has been carried out using many other analysis techniques such as FSEM, SIMS, TEM (HRTEM), UV/VIS and AES. (Niles, Herd & Al-Jassim, 1997; Bhushan & Sharma, 1992; Roenberg, et al., 1996; Dhere, et al., 1995). Also, this characterisation and analysis by various research groups using different investigative techniques has shown a similar composite picture of the structure and composition of these polycrystalline CBD \textit{CdS} thin films. Some investigative techniques and observed results are summarised in Table 2.1-1.
Table 2.1-1 Some analysis methods used and general observations or operations achieved.

<table>
<thead>
<tr>
<th>Method</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRD</td>
<td>Cubic and hexagonal structures revealed. Preferred orientation of hexagonal structures along the C axis (perpendicular to substrate) after annealing with temperatures &gt; 350°C. Hexagonal structure appears to be the higher temperature preferred structure. (Kaur, Pandya &amp; Chopra, 1980; Bhushan &amp; Sharma, 1992; Nair, et al., 1993; Jayakrishnan, et al., 1996; Gluszak, 1996)</td>
</tr>
<tr>
<td>RBS</td>
<td>Bulk composition ratios of cadmium to sulfur shown to vary depending on initial concentrations of Cd(^{2+}) and S(^{2-}) precursors. For creation of good quality polycrystalline films (type A) a ratio of approximately 1 to 1 is desirable. (Sahu, 1995).</td>
</tr>
<tr>
<td>ESCA</td>
<td>Surface composition show ratios of cadmium to sulfur can vary. Individual elements (Cd, S, O, C) found on near surface. Oxides found on and near surface. Sulphides found on surface as well as carbon and hydroxides. (Danaher, Lyons &amp; Morris, 1985; Rieke &amp; Bentjen, 1992; Nair, et al., 1993; Jayakrishnan, et al., 1996; Niles, Herd &amp; Al-Jassim, 1997).</td>
</tr>
<tr>
<td>SEM</td>
<td>Grain structure exhibited on surface of CdS film. Grain size varies with type of CBD technique used. Typical diameter of 10 to 20 nm grain size observed. (Dhere, et al., 1995; Gluszak, 1996; Tsuji, et al., 2000)</td>
</tr>
<tr>
<td>SIMS</td>
<td>Prominent peaks from S, S(_2), S(_3), CdS, CdO with smaller traces of organic material fragments from thiourea such as CN, CN(_2), CN(_3)H(_2), CNS. Small traces of CdOH and S(_3) identified. (Danaher, Lyons &amp; Morris, 1985)</td>
</tr>
<tr>
<td>UV/VIS</td>
<td>Band gap of CdS varies from 2.42 eV to 2.64 eV for pre-annealed to annealed films (&gt; 350°C). (Melo, et al., 1994; Dhere, et al., 1995; Gluszak, 1996)</td>
</tr>
<tr>
<td>AFM</td>
<td>Grain size measurement. Film thickness measurement. (Gluszak, 1996)</td>
</tr>
</tbody>
</table>

The two different types of CdS thin films (type A and type B) reported by the above researchers and many other groups are explained as follows:

As with different deposition methods, the CBD method results in the arrival of mobile deposit atoms / ions / molecules on the surface of a substrate, the mode of growth being
classified according to the way in which these atoms/ions/molecules arrange themselves and aggregate. There are three modes of growth classification and they are: monolayer growth; nucleated growth and nucleated growth following monolayer formation. All three modes of growth have been observed with the CBD method. Also, different process parameters associated with a particular method of CBD can have a dramatic effect on the films mode of growth e.g. an accelerated rate of nucleated growth of CdS films is caused by an increase in deposition temperature, as well, by increased concentrations of the deposition species $Cd^{2+}$ or $S^{2-}$ in solution (Gluszak & Hinckley, 2001). More importantly, experimenters have shown that one process parameter in particular can determine the actual type of film formed (Kaur, Pandya & Chopra, 1980). When a suspension of cadmium hydroxide $Cd(OH)_2$ is present in solution, the resulting deposition will form type A films, the $Cd(OH)$ acting as a catalyst by first attaching to a suitable surface with its $OH^-$ ligand.

The scientific literature indicates that with the correct initial conditions, the film grows initially by an ion-by-ion condensation of the depositing species $Cd^{2+}$ and $S^{2-}$ at preferred nucleation sites. As the reactions proceed, colloidal particles of $CdS$ also adhere to the substrate surface (described by ‘nucleation following monolayer formation’ growth). These colloidal particles continue to grow in all dimensions as deposition continues and form the particulate part of the film (Sebastian & Hu, 1994). The end of the deposition process is deemed when the colloidal particles are actually seen to be precipitating directly out into the solution, though this end phase of the deposition process can be delayed by the use of an appropriate buffer system (Dhere, et al., 1995).
Compounds of cadmium acetate \( Cd(CH_3COO)_2 \), cadmium chloride \( CdCl_2 \) and cadmium sulfate \( CdSO_4 \) have all been used for the creation of \( Cd^{2+} \) whereas thiourea \( CS(NH_2)_2 \) appears to be the primary source for the creation of \( S^{2-} \).

It appears that nucleated cubic grains or nucleated hexagonal grains of \( CdS \) can dominate the film and that this prominence of cubic structures or hexagonal structures is determined by the presence or absence of \( Cd(OH)_2 \) in solution during deposition. There is no evidence to state whether or not a single grain contains both cubic and hexagonal structures. Research has indicated that these grains appear to be forming in layers (2 or 3) with each layer exhibiting a different density that could be due to different grain sizes and different void sizes between adjacent grains. The apparent layers could also be a result of the analysis technique used and instead it is possible that a gradual change of density exists within the film.

Oxygen is diffused throughout the thin film and is an inherent product of the CBD method. This diffused oxygen is a major factor in the \( CdS \)'s high resistivity and is due to the abundant defect locations that oxygen creates. The oxygen can be eliminated via different techniques, but the easiest method appears to involve a rapid heating (approx. 400 °C) in a vacuum for a short duration of time. This method gives the advantages of annealing; hexagonal structures become dominant with an associated grain size enlargement; a major portion of the oxygen is removed (defect locations eliminated); and a small fraction of oxygen combines with cadmium to form cadmium oxide which lowers the resistivity of polycrystalline \( CdS \) thin film. This quick annealing technique also avoids the disadvantages of damage to the \( CdS \) crystalline structure, due to prolong heating.
Chapter 3 Theoretical Framework

Semiconductors, including CdS, are extremely important to the electronics industry and in turn, are of great importance to society, because without them we would not have the majority of appliances that we take for granted. Most of the electronic devices today are manufactured using processes and techniques derived from previous research and development initiatives from all around the world. Continued investigations of semiconductor atomic structure and semiconductor theory are of prime importance for future research and development. In order to understand how and why these devices function, this chapter introduces the reader to the basics of semiconductor theory, which includes CdS, and the theory of CdS atomic structural growth in relation to CBD.

3.1 General Film Growth

There are three main modes of growth classification to describe the formation of structures on the surface of another material as shown in Figure 3.1-1, and they are

I. Monolayer growth.
II. Nucleated growth.
III. Nucleation following monolayer formation.

Figure 3.1-1 Film growth processes
Monolayer growth occurs when the deposit species are bound more strongly to the substrate than they are to each other (Pashley, 1990). This results in the formation of monolayer islands of the deposit species which enlarge as deposition continues until a complete monolayer over the surface of the substrate has occurred. New monolayer islands then form on the first monolayer which also grow in size and merge together as deposition continues. The resulting deposit thus grows monolayer by monolayer. Alternating monolayers can be different depositing species so that formation of crystalline heterogeneous compounds occurs.

Nucleated growth occurs when the binding of the depositing species to each other is greater than to the substrate. The result is that the initial deposit species aggregate as small three dimensional islands, growing in all three dimensions, as the deposition continues. Depending on the presented depositing species, these aggregates can be heterogeneous compounds.

Nucleation following monolayer formation occurs when a small number of monolayer form (described by monolayer growth), with subsequent nucleation of three dimensional islands (described by nucleation growth) on top of these monolayers. These aggregates can also be heterogeneous compounds.

3.2 Crystal Structure

Irrespective of how film growth occurs, when compounds are examined at the atomic / molecular level, structures can be discerned in most compounds and can be classified as either Crystalline (see Figure 3.2-1)
Figure 3.2-1 Crystalline structure displaying periodic arrangement of the atoms/molecules.

or Polycrystalline. Polycrystalline materials display many small regions (grains/sheets) of the same crystalline material but the orientations of each grain / sheet can be different from one another as shown in Figure 3.2-2

Figure 3.2-2 Polycrystalline structure of material shows interconnecting crystalline sections.

When no structure can be found the material is said to be Amphorus (see Figure 3.2-3).

Figure 3.2-3 Amphorus material showing random arrangement of atoms/molecules.
When examining a crystalline material, the atoms making up the crystal are seen to be arranged in a periodic lattice, with some basic arrangement of atoms (called the unit cell) that is regularly repeated throughout the entire solid. Basis vectors can be defined \((a, b, c,\ldots)\) such that if the unit cell is translated by integral multiples of these vectors, a new, identical unit cell is found. This translation is expressed as \(r = pa + qb + sc\). (see Figure 3.2-4)

![Figure 3.2-4 A two-dimensional lattice showing translation of a unit cell by \(r = 9a + 3b\)](image)

A classification table of the possible structures found in crystalline materials is presented, describing seven crystal systems in 3 dimensional lattice space (see Table 3.2-1 with definition Figure 3.2-5). Associated with this table are the corresponding labeled diagrams shown in Figure 3.2-6.
### Table 3.2-1 Classification table of structures found in crystalline materials.

<table>
<thead>
<tr>
<th>System</th>
<th>Bravais Lattice</th>
<th>Characteristic Bulk Symmetry Element</th>
<th>Unit Cell Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>Simple</td>
<td>None</td>
<td>$a \neq b \neq c$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\alpha \neq \beta \neq \gamma \neq 90^\circ$</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>Simple</td>
<td>One 2-fold rotation axis</td>
<td>$a \neq b \neq c$</td>
</tr>
<tr>
<td></td>
<td>Base-centred</td>
<td></td>
<td>$\alpha = \beta = 90^\circ \neq \gamma$</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>Simple</td>
<td>Three mutually perpendicular 2-fold rotation axis</td>
<td>$a \neq b \neq c$</td>
</tr>
<tr>
<td></td>
<td>Base-centred</td>
<td></td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td></td>
<td>Body-centred</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Face-centred</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cubic</td>
<td>Simple</td>
<td>Four 3-fold rotation axes</td>
<td>$a = b = c$</td>
</tr>
<tr>
<td></td>
<td>Body-centred</td>
<td>(cube diagonals)</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td></td>
<td>Face-centred</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetragonal</td>
<td>Simple</td>
<td>One 4-fold rotation axis or a 4-fold rotation-inversion axis</td>
<td>$a = b \neq c$</td>
</tr>
<tr>
<td></td>
<td>Body-centred</td>
<td></td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>Simple</td>
<td>One 6-fold rotation axis</td>
<td>$a = b \neq c$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\alpha = 120^\circ \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>Trigonal</td>
<td>Simple</td>
<td>One 3-fold rotation axis</td>
<td>$a = b = c$</td>
</tr>
<tr>
<td>(Rhombohedral)</td>
<td></td>
<td></td>
<td>$\alpha = \beta = \gamma \neq 90^\circ$</td>
</tr>
</tbody>
</table>

**Figure 3.2-5** Unit cell with definitions
The importance of the unit cell lies in the fact that the crystal can be analysed as a whole simply by investigating a representative volume. The actual dimensions of the unit cell (lattice constants) are of great interest to most investigations as calculations of structure and density can be made if these constants are resolved. In particular the determination of the packing factor (ratio of the occupied volume of the atoms present in the unit cell to the total volume of the unit cell) can be used to determine the possible position of impurities within the unit cell. There are 14 basic unit cells in 3 dimensions called Bravais lattices and these are shown in Figure 3.2-6.

Figure 3.2-6. Bravais lattices represented by fourteen basic unit cells in 3 dimensions.
Of special interest are the Cubic and Hexagonal structures, as these have been previously identified in CBD CdS thin films (see Figure 3.2-7).

![Simple cubic and Hexagonal structures](image)

**Figure 3.2-7** Cubic and Hexagonal structures found in CdS thin films.

When describing these structures, points of standard reference are required such as *planes* and *directions* within the lattice.

### 3.2.1 Miller Indices

*Miller indices* are a set of three integers used to describe the position of a plane within the lattice. These three integers that describe a particular plane are calculated by three steps (Streetman & Banerjee, 2000, p.7).

1. Find the intercepts of the plane with the crystal axes and express these intercepts as integral multiples of the basis vectors (the plane can be moved in and out from the origin, retaining its orientation, until such an integral intercept is discovered on each axis).
II. Take the reciprocals of the three integers found in step I. and reduce these to the smallest set of integers \( h, k \) and \( l \), which have the same relationship to each other as the three reciprocals.

III. Label the plane in parentheses \((hkl)\).

This procedure is shown by way of an example using Figure 3.2.1-1. The plane has intercepts at \( 3a \), \( 4b \), and \( 2c \) along the three axes. Taking the reciprocals of these intercepts, we obtain \( \frac{1}{a} \), \( \frac{1}{b} \), and \( \frac{1}{c} \). These reciprocals are then multiplied by 12 to obtain the Miller indices \((436)\).

![Figure 3.2.1-1 A crystal plane represented by Miller indices (436)](image)

One advantage of taking the reciprocals of the intercepts is the avoidance of infinities in the notation (i.e. for a plane parallel to an axis the intercept would be infinity but its reciprocal is simply taken as zero.) Any plane passing through the origin can be translated to a parallel position for calculation of the Miller indices and if an intercept occurs on the negative branch of an axis, a minus sign is placed above the Miller index - i.e. \((-hkl\)). The following 3 diagrams shown in Figure 3.2.1-2 are examples of planes observed in lattices.
Figure 3.2.1-2 Three sets of planes. Each individual plane pertaining to a set has the same miller indices. (Callister, 2000).

Many planes with given Miller indices in a lattice are equivalent simply by choice of position and orientation of the unit cell, so the indices of these equivalent planes are braced {} instead of using parentheses (eg. {100}) for a cubic lattice as all the faces can be rotated in various directions and still appear the same (see Figure 3.2.1-3).
3.2.2 Direction Vectors

The direction in a lattice is also used to describe the unit cells orientation and is expressed as a set of three integers, enclosed in square brackets, with the same relationship as the components of a vector in that direction. Expressed in multiples of the basis vectors, the three vector components are reduced to their smallest values while retaining their relationship (see Figure 3.2.1-4).

Figure 3.2.1-4 Crystal directions in the cubic lattice.

(Streetman & Banerjee, 2000).
And as in the case of planes, many directions in a lattice are equivalent, depending only on
the arbitrary choice of orientation for the axes. These equivalent direction indices are
placed in angular brackets ⟨ ⟩.

3.3 Solid State Physics

To understand how semiconductors function it is necessary to understand the basics
from which semiconductor theory is derived and so a start is made with the photoelectric
effect, from which so many other important discoveries have been made.

3.3.1 The Photoelectric Effect

This effect, first observed by Plank, indicated that electromagnetic radiation is emitted
or absorbed in discrete units of energy, called quanta. These energy units are described by
the formula

\[ E = hv \]

where \( v \) (Hz) is the frequency of the radiation and \( h \) \( (h = 6.63 \times 10^{-34} \text{ J-s}) \) is a quantity now
called Plank’s constant. When monochromatic light (photons of the same energy) is
incident on the surface of a metal it is possible for some electrons to be ejected away from
the metals surface as shown in Figure 3.3.1-1.

![Figure 3.3.1-1 Ejected electron caused by incident photon striking metal surface.](Streetman & Banerjee, 2000).
This will only happen if the individual photons have enough or more energy (governed by $E = h\nu$) to overcome the work function ($q\Phi$) of the metal. By employing a simple technique to measure the energy of the escaping electrons, a graph (see Figure 3.3.1-2) can be made of the maximum energy ($E_m$) as a function of the frequency ($\nu$) of the incident light and is described by the formula

$$E_m = h\nu - q\Phi \quad [3.3.1-2]$$

where $h$ is derived from the slope of the graph and its $E_m$ intercept is equal to the work function of the particular metal used. This experiment clearly demonstrates that Plank's original hypothesis was correct, that light energy is contained in discrete units.

3.3.2 Line Spectra

From the analysis of atomic spectra it becomes apparent that electrons surrounding an atom can only change their energy positions in discrete units. Emission line spectra series are grouped and named (Lyman, Balmer, and Paschen) after the scientists responsible for first discovering these different series (see Figure 3.3.2-1).
The initial attempt to explain the results of atomic line spectra was forwarded by Niels Bohr, who constructed a model (see Figure 3.3.2-2) for the hydrogen atom based on the mathematics of planetary systems.

Figure 3.3.2-1 Relationships among photon energies in the hydrogen spectrum.

(Streetman & Banerjee, 2000).

Figure 3.3.2-2 The Bohr model of the hydrogen atom depicting electron orbits and transitions.
3.3.3 Bohr Model

In order to make his model work, Bohr had to make some postulates:

- Electrons exist in certain stable, circular orbits about the nucleus and do not give off radiation, contrary to classical electromagnetic theory which requires the electrons to continuously radiate energy whilst under the influence of angular acceleration.
- Electrons may shift to higher or lower orbits, gaining or losing energy equal to the difference in the energy levels. This allowed energy change would be by the absorption or emission of a photon of energy $hv$.
- The angular momentum $p_0$ of the electron in an orbit is always an integral multiple of Planck's constant divided by $2\pi$ and is a necessary assumption to obtain the observed experimental results discovered by Lyman, Balmer and Paschen. (Streetman & Banerjee, 2000).

Although the Bohr model was a great step forward for describing the gross features for electronic transitions within the atom, it had its limitations:

- It could only be successfully applied to the hydrogen atom and the single electron ions such as the Helium ion ($He^+$), the Lithium ion ($Li^{++}$), etc.
- It was not able to account for the intensities or the fine structure of the spectral lines.
- It could not explain the binding of atoms into molecules.

The success of the theory was that it forwarded the concept that electrons are quantized in certain allowed energy levels and that the difference in these energy levels can be described as

$$ hv = E_2 - E_1 \quad \text{[3.3.3-1]} $$

With the realisation that the Bohr model was not sufficient to explain all experimental data, other models were developed. Two different mathematical methods (Schrödinger wave...
mechanics and Heisenberg's matrix mechanics), which in actuality share the same basic principle, independently produced the principles of quantum mechanics that is now call quantum theory. (Streetman & Banerjee, 2000).

3.3.4 Quantum Model

Quantum theory deals with the atomic scale and describes the probabilistic nature of events involving atoms and electrons. The mathematics shows that the Heisenberg's uncertainty principle of position and momentum

$$\Delta x \Delta p_x = \frac{\hbar}{2}$$

and the uncertainty of energy and time

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

directly support the quantum model. When dealing at the atomic scale, simultaneous measurement of position and momentum or of energy and time are inherently inaccurate to some degree so instead, average values (expectation values / probability values) are used.

One of the important results of quantum mechanics is that a probability density function can be obtained for a particle (ie. an electron) in a certain environment. This function can be used to find the expectation value of quantities such as momentum, position, and energy within the limits of the uncertainty principle.

Quantum theory can represent an electron as a wavefunction and interactions between electrons can be predicted by interfering wavefunctions. Quantum theory predicts that the electron states in atoms have discrete energy levels and that the lowest energy cannot be zero. The derived equation (Thornton & Rex, 1993)

$$E_n = n^2 \frac{\pi^2 \hbar^2}{2mL^2} \quad n = 1, 2, 3, \ldots$$
shows that quantization of the energy occurs in a natural way from the application of the boundary conditions (standing waves) to possible solutions of the electron wave equation. The diagrams in Figure 3.3.4-1 refer to a single isolated particle that would have a potential well with infinite walls as barriers.

![Wave functions and energy levels](image)

**Figure 3.3.4-1** Wave functions $\Psi_n$, probability densities $|\Psi_n|^2$, and energy levels $E_n$ for the quantum numbers for the infinite square well potential. (Thorton & Rex, 1993).

The wave functions are relatively easy to obtain for the potential well with infinite walls, since the boundary conditions force the waveform function ($\Psi$) to zero at the walls.

### 3.3.5 Band Theory of Semiconductors

When atoms are brought together to form a solid, various atomic interactions occur among the neighbouring atoms. These interactions are crystal vibrations (known as phonons); coulomb attraction and repulsion forces; and electronic wavelength overlap (interference). These atomic forces of attraction and repulsion eventually equilibrate at a particular interatomic spacing for the crystal. This equilibrium of forces causes changes to occur in the electronic energy level configurations, which gives rise to characteristic electrical and optical properties.
When two atoms are isolated from one another, the electronic wave functions are considered as non-interacting and they will have identical electronic structures. But when these two atoms are brought close together they interact with one another via the coulomb attraction and repulsion forces and their respective wave functions overlap. Because no two electron wave functions can have the same quantum state (Pauli Exclusion Principle) a splitting of each atom's discrete energy level occurs, resulting in new energy levels that are exclusive to the particular atom combination. (Thorton & Rex, 1993)

In a real solid, many atoms are in close proximity to one another resulting in many overlapping wave functions. These overlapping wave functions result in further splitting of energy levels to the point where continuous energy bands become apparent as shown in Figure 3.3.5-1.

![Figure 3.3.5-1](image)

Figure 3.3.5-1 The 1s and 2s energy-level splitting of 13 hydrogen atoms in close proximity, resulting in the splitting of each energy level into a nearly continuous band.
The above diagrams only show two energy bands but for most atoms there are a large number of possible energy bands. The two most important energy bands are called the conduction band and the valence band.

These two bands are primarily responsible for the types of bonding occurring between atoms and the conductivity of the material. Every solid has its own characteristic energy band structure and this variation in band structure is responsible for the wide range of electrical characteristics observed in insulators and semiconductors. The upper-most band is called the conduction band \((CB)\), defining the allowed electron states within the solid. These electrons are bound loosely to the lattice of the solid. The lower band is called the valence band \((VB)\), representing the energy states of the valence electrons which form covalent bonds that define the structure of the solid. Both bands are separated by a region called the energy band gap \((E_g)\) where no allowed electron states exist, as shown above in Figure 3.3.5-1 and in the standard form in Figure 3.3.5-2.

![Figure 3.3.5-2 Standard representation of band structure resulting from many atoms having overlapping wave functions.](image)

The band structures of insulators and semiconductors closely resemble each other, the basic difference being that semiconductors have a much smaller energy band gap. If the material is an insulator then its energy gap is large (several electron volts) making it too difficult for an applied field to move electrons from the valence band to the conduction
band. But in a semiconductor, it is much easier to excite electrons from the valence band to the conduction band by simple means such as vibration or optical excitation (see Figure 3.3.5-3).

![Diagram of energy gap between insulator and semiconductor](image)

**Figure 3.3.5-3** Difference in energy gap between an insulator and a semiconductor.

Thus an important difference between semiconductors and insulators is that the number of electrons available for conduction can be greatly increased in semiconductors by thermal or optical energy. Another important effect resulting from the different energy bands for different semiconductors materials is whether the bands are direct (vertical transition) or indirect (transverse transition).

### 3.3.6 Direct and Indirect Energy Transitions

The type of energy transition that an electron can experience when moving between bands is directly related to whether the semiconductor is direct or indirect.

In the first graph labeled Direct (see Figure 3.3.6-1), the conduction band minimum and the valence band maximum share the same $k$ value. An electron making a smallest-energy transition from the conduction band to the valence band or visa versa can do so without a change in the $k$ value.
The two diagrams of electron energy versus $k$ ($k = 2\pi / \lambda$) represent two different materials with associated energy bands and bang gaps:

(a) direct translation with accompanying photo emission

(b) indirect translation via a defect level

(Streetman & Banerjee, 2000).

In the second graph labeled Indirect (see Figure 3.3.6-1), the valence band maximum is at a different $k$ value than that of the conduction band minimum. For a smallest-energy transition from the conduction band to the valence band or visa versa to occur a change in the $k$ value is required, which requires a change of momentum for the electron. Therefore another way of interpreting the above diagrams is to view them as Electron energy versus momentum plots, with a scaling factor of $\hbar$. In a direct transition, where an electron moves from the conduction band to an empty state in the valence band, the energy difference $E_g$ is given off as a photon. In an indirect transition where an electron moves from the conduction band to an empty state in the valence band, which involves changes in $k$ (momentum), the energy is generally given up as heat to the lattice rather than as an emitted photon.
To properly examine the behaviour of electrons within the lattice using quantum mathematical methods would require too much computation using computers to be of any practical use. Fortunately there is a method that allows the use of classical formula in conjunction with a derived unit called effective mass (\( m^* \)) which simplifies required calculations and allows insightful formulations of semiconductor theory.

### 3.3.7 Effective Mass

Electrons that are in the conduction band are relatively free to move under the influence of any applied electric field (\( \xi \)). In order to understand what is happening to these electrons, an energy - momentum relationship is first derived for a non-relativistic electron moving in free space using de Broglie’s relation \( p = mv = \hbar k \).

The equation [3.3.7-1] shows the electron energy is parabolic with wave vector \( k \) and by taking the second derivative with respect to \( k \), equation [3.3.7-2] is obtained.

\[
E = \frac{1}{2}mv^2 = \frac{1}{2} \frac{p^2}{m} = \frac{\hbar^2}{2m} k^2
\]  

[3.3.7-1]

This equation shows that the electron mass is inversely related to the curvature of the \( E(k) \) relationship.

Although electrons in solids are not free, most energy bands are generally parabolic at their extrema (minima for conduction bands and maxima for valence bands) and an approximate effective mass (\( m^* \)) can be calculated for these maxima and minima positions from the curvature of these bands. (Streetman & Banerjee, 2000).
Rearranging equation [3.3.7-2] results in equation [3.3.7-3] for effective mass:

\[ m^* = \frac{\hbar^2}{d^2E/dk^2} \]  [3.3.7-3]

An important feature of the effective mass equation is that curvature of the conduction band minima is positive but at the valence band maxima this curvature is negative. It is important to realise that this effective mass relates to the gross behaviour of the electron, taking into account all quantum effects, and is not simply an altered mass unit. The result is that valence band electrons with negative charge and negative mass move in an electric field in the same direction as holes with positive charge and positive mass.

3.3.8 Holes

The motion of charged particles is not confined to electrons moving with positive effective mass in the conduction band, but also to electrons moving with negative effective mass in the valence band. When an electron is excited into the conduction band, it leaves behind an empty state (vacancy) in the valence band that is called a hole \( h^+ \). This hole is treated as if it really is a particle with a positive charge moving under the influence of an electric field in the positive direction, but in reality is the resultant effect of a valence band electron with negative effective mass moving in the same positive direction. The excitation of valence band electrons to the conduction band results in the creation of conduction band electrons and valence band holes, collectively called electron-hole pairs (EHP). What effect these electron-hole pairs have on a semiconductor material can be seen when intrinsic and extrinsic semiconductors are examined.

3.3.9 Intrinsic and Extrinsic Semiconductors

A perfect semiconductor crystal with no impurities or lattice defects is called an intrinsic semiconductor. In such a material there are no charge carriers at temperature 0 Kelvin, since the valence band is filled with electrons and the conduction band is empty.
At higher temperatures electron-hole pairs are generated as valence band electrons are excited thermally across the band gap to the conduction band. Because these electron-hole pairs are the only charge carriers in the intrinsic material, the conduction band electron concentration \( n \) (electrons per cm\(^3\)) is equal to the concentration of holes in the valence band \( p \) (holes per cm\(^3\)). Each of these intrinsic carrier concentrations is commonly referred to as \( n_i \) and are related by the formula (Streetman & Banerjee, 2000).

\[
n = p = n_i
\] [3.3.9-1]

If the conduction band maintains a certain concentration of electron-hole pairs at a given temperature \( n_i \), then the generation rate \( g_i(T) \) (\( EHP/cm^3 \) per sec) of these electron-hole pairs must be equaled by the recombination rate \( r_i(T) \) (\( EHP/cm^3 \) per sec) as shown with the formula

\[
g_i(T) = r_i(T)
\] [3.3.9-2]

A temperature increase results in a new carrier concentration \( n_t \) as well as an increased recombination rate to balance the increased generation rate. It follows that for any temperature, the rate of recombination of electrons and holes is proportional to the equilibrium concentration of electrons and holes, as shown by the formula:

\[
r_i = \alpha_r n_0 p_0 = \alpha_r n_i^2 = g_i
\] [3.3.9-3]

where \( \alpha \) is a proportionality constant and depends on the manner by which recombination occurs. Now, by adding impurity atoms into the perfect crystal it is possible to create additional carriers in the semiconductor. This process, called doping, can produce additional energy band levels, usually within the energy band gap. This modification produces an extrinsic semiconductor, which by choice, can predominate with either electrons or holes. If electrons are made the dominant charge carrier by doping, the material is called a \( n \)-type semiconductor and if holes are made the dominant charge
carrier, then the material is called a \( p \)-type semiconductor. It can be seen from Figure 3.3.9-1 that the extrinsic material majority carrier concentration \( n_e \) is significant and fairly constant for a range of temperatures. The dashed line indicates the carrier concentration for the non-doped (intrinsic) semiconductor material and highlights the large difference in carrier concentrations for both types of material.

![Figure 3.3.9-1](image)

Figure 3.3.9-1 Carrier concentration verses inverse temperature for a doped semiconductor (Streetman & Banerjee, 2000).

How doping can produce \( n \)-type or \( p \)-type extrinsic semiconductors is shown by way of an example from Streetman and Banerjee, (2000). Doping a group IV (periodic table) semiconductor (i.e. silicon, Si) with group V atoms (P, As, and Sb) introduces an energy level very close to the conduction band in the energy band gap. This energy level is filled with electrons at temperature 0 Kelvin and requires very little thermal energy (50 – 100 Kelvin) to excite electrons across the reduced energy gap to the conduction band as shown.
in Figure 3.3.9-2. These impurity atoms are called \textit{donor} atoms and are responsible for creating the $n$-type semiconductor.

\begin{center}
\includegraphics{diagram1.png}
\end{center}

\begin{center}
\includegraphics{diagram2.png}
\end{center}

\begin{center}
\includegraphics{diagram3.png}
\end{center}

\begin{center}
\includegraphics{diagram4.png}
\end{center}

Figure 3.3.9-2 Energy band model of donor atoms in semiconductors.

(Streetman & Banerjee, 2000).

When large numbers of donor atoms ($N_d$) are used such that the intrinsic levels of electrons and holes become insignificant, the majority carrier concentration can be written as:

$$n_0 = N_d \langle n_i, p_o \rangle \quad \text{at room temperature} \quad [3.3.9-4]$$

Similarly, group III atoms ($B, Al, Ga, In$) introduce energy levels close to the valence band in group IV semiconductors. At low temperatures (50 – 100 Kelvin), electrons are thermally excited from the valence energy band into the impurity energy level leaving a vacancy (hole) in the valance energy band (see Figure 3.3.9-3). These impurity atoms are called \textit{acceptor} atoms and are responsible for creating the $p$-type semiconductor.
Doping with significant numbers of acceptor atoms causes the hole concentration \( (p_0) \) to be greater than the conduction band electron concentration \( (n_0) \) and can be expressed as

\[
p_0 = N_a >> (n_0) \quad \text{at room temperature.} \tag{3.3.9-5}
\]

When a semiconductor is doped \( n \)-type, electrons dominate and are called the majority carriers while the holes are called the minority carriers. Similarly, when a semiconductor is doped \( p \)-type, holes dominate and are called the majority carriers while the electrons are called the minority carriers. The type and amount of doping within a semiconductor determines its electrical properties and therefore doping concentration calculations are an important aspect.

3.3.10 Electron and Hole Concentrations

When calculating semiconductor electrical properties and analyzing device behaviour, it is often necessary to know the number of charge carriers per \( \text{cm}^3 \) in the material. To obtain equations for the carrier concentrations, investigation is required of the distribution of carriers over the available energy states at thermal equilibrium, by using the statistically derived Fermi-Dirac distribution function.
\[ f(E) = \frac{1}{1 + e^{\frac{E-E_F}{kT}}} \]  \hspace{1cm} [3.3.10-1]

Where \( k \) is Boltzmann’s constant, \( T \) is absolute temperature and \( E_F \) is the Fermi level. This function gives the probability that an available energy state at \( E \) will be occupied by an electron at absolute temperature \( T \). The probability value of a half \( (f(E) = \frac{1}{2}) \) is calculated for finding an electron at an energy level \( E \) equal to the Fermi energy level (see Figure 3.3.10-1).

![Figure 3.3.10-1 The Fermi-Dirac distribution function.](Streetman & Banerjee, 2000).

The Fermi function value of one \( (f(E) = 1) \) shows that at 0 Kelvin every available energy state up to \( E_F \) is filled with electrons and all states above \( E_F \) are empty. At higher temperatures the Fermi function spreads out \( (T_1, T_2) \) its edges overlapping equally into the conduction band and the valence band. The symmetry of the distribution of empty and filled states about \( E_F \) makes the Fermi level a excellent reference point in calculations of electron and hole concentrations in semiconductors. If there are no available states at \( E \), as in the energy band gap \( E_g \) of a semiconductor, then there is no possibility of finding an electron there. For an intrinsic material, the concentration of holes in the valence band is
equal to the concentration of electrons in the conduction band and therefore, the Fermi level $E_F$ must lie at the centre of the band gap.

In $n$-type material there is a high concentration of electrons in the conduction band and a low concentration of holes in the valence band. The outcome of this is that the Fermi level is shifted to a higher energy level above its intrinsic level. This results in the edges of the Fermi distribution overlapping more into the conduction band (increased probability of electrons being found in the conduction band) and less into the valence band.

In $p$-type material the Fermi level lies closer to the valence band so that the edges of the Fermi distribution function overlap more into the valence band, indicating that the probability of finding an electron in this band to be higher.

Concentrations of electrons and holes can be made by taking the integral of the Fermi distribution function and the density of available states $N(E)$ (available energy levels per cm$^3$ in the conduction band or valence band) with respect to energy. The concentration of electrons in the conduction band is calculated with equation [3.3.10-2].

$$n_0 = \int_{E_c}^{\infty} f(E)N(E)dE$$  \[3.3.10-2\]

The function $N(E)$ can be calculated using quantum mechanics and the Pauli exclusion principle and is found to be proportional to $E^{3/2}$. The outcome of all the mathematics is that most of the electrons will be found at the conduction band edge and most of the holes will be found at the valence band edge, so that an effective density of states $N_e$ for the conduction band and $N_v$ for the valence band can be used resulting in the two equations

$$n_0 = N_e f(E_c)$$  \[3.3.10-3\]

$$p_0 = N_v [1 - f(E_v)]$$  \[3.3.10-4\]
By making the assumption that the Fermi level $E_F$ lies at least several $kT$ (0.0259 eV) below the conduction band, the Fermi function $f(E_c)$ can be simplified so that the concentration equation for $n_0$ becomes

$$n_0 = N_c e^{-(E_F - E_c)/kT}$$  \[3.3.10-5\]

A similar assumption is made for the Fermi function $f(E_v)$ lying above the valence band so that the concentration equation for $p_0$ becomes

$$p_0 = N_v e^{-(E_F - E_v)/kT}$$  \[3.3.10-6\]

Formula [3.3.10-5] and [3.3.10-6] can be further manipulated to produce the equations

$$n_0 p_0 = n_i^2$$  \[3.3.10-7\]

$$n_0 = n_i e^{(E_F - E_i)/kT}$$  \[3.3.10-8\]

$$p_0 = n_i e^{(E_v - E_F)/kT}$$  \[3.3.10-9\]

Equations [3.3.10-8] shows that the electron concentration is $n_i$ when $E_F$ is at the intrinsic level $E_i$ and that $n_0$ increases exponentially as the Fermi level moves away from $E_i$ toward the conduction band. Similarly, equation [3.3.10-9] shows that the hole concentration is also $n_i$ when $E_F$ is at the intrinsic level $E_i$ and that $p_0$ increases exponentially as the $E_F$ moves away from $E_i$ toward the valence band.

3.3.11 Excess Carriers in Semiconductors

Most semiconductor devices operate by the creation of charge carriers in excess of the thermal equilibrium values and these excess charge carriers can dominate the conduction
processes. Excess charge carriers can be created by optical excitation, thermal vibration and direct injection methods.

3.3.12 Optical Absorption

An important technique for measuring the band gap energy of a semiconductor is the absorption of incident photons by the material. For absorption of the photon to occur its energy must be equal to or greater than the energy band gap $E_g$ of the semiconductor (see Figure 3.3.12-1). Also, for the transition to occur requires that the valance band contain available electrons and that the conductance band have available empty states.

Figure 3.3.12-1 Excitation of an electron into the conduction band and its subsequent decay. (Streetman & Banerjee, 2000).

(a) Transition of electron into conduction band after absorbing photon
(b) Energy lost due to lattice scattering
(c) Transition of electron to valence band

(Streetman & Banerjee, 2000).

Excited electrons might initially have more energy than is common for conduction band electrons and so will lose this extra energy to lattice scattering. The electron and hole created by the absorption of photon energy are excess carriers and will eventually
recombine. Whilst these excess carriers exist in their respective bands, they can contribute to the conductivity of the material.

3.3.13 Direct Recombination of Electrons and Holes

Electrons in the conduction band can make transitions to the valence band of a semiconductor (i.e. recombine with holes in the valence band) either directly or indirectly. In direct recombination, excess electrons and holes decay by electrons moving from the conduction band to empty states (holes) in the valence band. When a transition from a higher energy state (conduction band) to a lower energy state (valence band) occurs, energy lost by the electron is given up as a photon. Direct recombination is spontaneous and the probability of this process occurring is constant with time.

The net rate of change in the conduction band electron concentration $n_0$ is the thermal generation rate minus the recombination rate.

$$\frac{dn(t)}{dt} = \alpha \cdot n_t^2 - \alpha \cdot n(t) \cdot p(t)$$  \[3.3.13-1\]

If the initial excess electron $\Delta n$ and hole $\Delta p$ concentrations are equal (e.g. created from a burst of light where $h\nu \geq E_g$), then when they recombine in pairs, the instantaneous concentration of carriers $\delta n(t)$ and $\delta p(t)$ are also equal. The above equation can be rewritten as

$$\frac{dn(t)}{dt} = \alpha \cdot n_t^2 - \alpha \cdot [n_0 + \delta n(t)][p_0 + \delta p(t)]$$  \[3.3.13-2\]

and with rearranging where $\delta n(t) = \delta p(t)$

$$\frac{dn(t)}{dt} = -\alpha \cdot [(n_0 + p_0)\delta n(t) + \delta n^2(t)]$$  \[3.3.13-3\]
For low level injection (small excess carrier concentrations), the $\delta n^2(t)$ term can be neglected. Furthermore, if the material is extrinsic, the term representing the equilibrium minority carriers can be ignored (i.e. $p$-type material - $p_0 \gg n_0$) to obtain the equation:

$$\frac{d\delta n(t)}{dt} = -\alpha, p_0 \delta n(t)$$  \[3.3.13-4\]

The solution for this equation is an exponential decay of the initial excess carrier concentration $\Delta n(t)$ at $t = 0$ and is described by:

$$\delta n(t) = \Delta n \exp(-\alpha, p_0 t) = \Delta n \exp(-t / \tau_n)$$  \[3.3.13-5\]

The decay constant term $\tau_n = (\alpha, p_0)^{-1}$ in the above equation is the recombination lifetime, (minority carrier lifetime) for excess electrons in a $p$-type semiconductor. Similarly, the decay of excess holes in a $n$-type semiconductor occurs with $\tau_p = (\alpha, n_0)^{-1}$.

A more general expression for carrier lifetime that is valid for $n$-type or $p$-type semiconductors with the requirement of low level injection is

$$\tau_n = \frac{1}{\alpha, (n_0 + p_0)}$$  \[3.3.13-6\]

The semi-logarithmic graph in Figure 3.3.13-1 shows what is happening to the concentrations of holes and electrons in a $p$-type material after a low level injection of equal amounts of excess electrons and holes.
Figure 3.3.13-1 Decay of excess electrons and holes by recombination.

The hole majority carrier concentration remains relatively static whilst the electron minority carriers are decaying linearly (representing exponential decay).

3.3.14 Indirect Recombination and Trapping

With indirect recombination in an extrinsic material, a majority of the recombination events occur via recombination levels within the energy gap and subsequently the carrier lifetime is more complicated than is the case for direct recombination.

This smaller transition of the electron, when moving from the conduction band to this intermediate recombination level, results in the energy loss being given up as heat to the lattice. Any impurities or lattice defects act as recombination centres and are able to receive one type of carrier whilst capturing the other, resulting in the annihilation of the pair. Another effect these impurities and lattice defects can produce is called trapping. This occurs when a carrier is temporarily trapped and then re-excited without recombination taking place.
Direct measurement of the semiconductors photoconductive decay characteristics (voltage variations across carrier injected semiconductor versus time) is a convenient method for determining the effects of recombination and trapping within an extrinsic material.

\[ \sigma(t) = q[n(t)\mu_n + p(t)\mu_p] \]  

[3.3.14-1]

where \( \sigma(t) \) (\( \Omega \cdot \text{cm} \))\(^{-1} \) is the conductance of the semiconductor and \( \mu_n \) and \( \mu_p \) are mobility's (\( \text{cm/s}/(\text{V cm}) = \text{cm}^2/(\text{V.s}) \)) of electrons and holes in a lattice respectively. By recording the sample resistance as a function of time, the actual carrier's lifetimes can be determined.

3.3.15 Conductivity and Mobility

Charge carriers in a solid are in constant thermal motion, being the result of random scattering from lattice vibrations, impurities, other charge carriers and defect centres. When an electric field \( \xi_x \) is applied in the \( x \)-direction, each electron experiences a net force of \( -q\xi_x \) and the average momentum \( \langle p_x \rangle \) per electron of a group of \( n \) electrons/cm\(^3\) is calculated to be

\[ \langle p_x \rangle = \frac{p_x}{n} = -q\bar{t}\xi_x \]  

[3.3.15-1]

where \( \bar{t} \) represents the mean free time between electron scattering events.

From the above momentum equation, the average constant velocity (net drift) in the negative \( x \)-direction is shown to be

\[ \langle v_x \rangle = \frac{\langle p_x \rangle}{m^*} = -\frac{q\bar{t}}{m^*}\xi_x \]  

[3.3.15-2]

where \( m^* \) is the conductivity effective mass for electrons (different from the density of states effective mass). (Streetman & Banerjee, 2000).
The current density resulting from this net movement of electrons in the negative x-direction is given by the equation [3.3.15-3].

\[ J_x = -qn\langle \nu_x \rangle = \frac{nq^2 \bar{t}}{m_n} \xi_x \]  \hspace{1cm} [3.3.15-3]

where \(\mu_n\) is the electron mobility and indicates the ease with which electrons drift through a particular material.

From Ohm's law, current density is proportional to the electric field.

\[ J_x = \sigma \xi_x \]  \hspace{1cm} [3.3.15-4]

where \(\sigma = \frac{nq^2 \bar{t}}{m_n}\)

and conductivity can be expressed as

\[ \sigma = qn\mu_n \]  \hspace{1cm} [3.3.15-5]

where \(\mu_n = \frac{\bar{t}}{m_n}\)

The electron mobility \(\mu_n\) is a very important quantity in characterizing semiconductor materials and can be expressed as the average particle drift per unit electric field.

\[ \mu_n = \frac{\langle \nu_x \rangle}{\xi_x} \]  \hspace{1cm} [3.3.15-6]

Because electrons drift in the opposite direction to the electric field, the minus sign in the above equation results in a positive value of mobility. This allows the current density due to electron conduction to be written as

\[ J_x = qn \mu_n \xi_x \]  \hspace{1cm} [3.3.15-7]

and the current density due to hole conduction to be written as

\[ J_x = qn \mu_p \xi_x \]  \hspace{1cm} [3.3.15-8]

Thus the total current density due to both electron and hole conduction is expressed as
Current density is one of the quantities that describes how charge carriers tend to move under the influence of an electric field in a semiconductor. Another important quantity that also describes the movements of charge carriers, but without the need for an electric motive force, is diffusion. (Streetman & Banerjee, 2000).

3.3.16 Diffusion

If excess carriers are created in one part of a semiconductor (i.e. direct injection or optical excitation in one part of the semiconductor ) resulting in a high concentration of carriers in that area, the electrons and holes tend to move away into areas where there is a lower concentration of carriers. This unequal carrier concentration distribution is called a carrier gradient and the type of carrier motion it produces is called diffusion. Diffusion of carriers represents one of the two basic processes of current conduction in semiconductors, the other process being drift current due to an electric field. Carriers in a semiconductor diffuse in a carrier gradient by random thermal motion and scattering from the lattice and impurities. The graph of Figure 3.3.16-1 shows how the carrier concentration spreads out over the one dimensional x-direction with respect to time.
Figure 3.3.16-1 Spreading of a pulse of electrons with respect to time.

(Streetman & Banerjee, 2000).

By segmenting one side of the electron concentration gradient into lengths equal to the mean free path $\bar{l}$ between collisions, the one dimensional electron flux density $\Phi_n$ equation is formulated

$$\Phi_n(x_0) = \frac{\bar{l}}{2\bar{t}} (n_1 - n_2)$$  \[3.3.16-1\]

where $\bar{l}$ represents the mean free path between electron scattering events, $\bar{t}$ represents the mean free time between the collisions and $(n_1 - n_2)$ is the difference in electron concentration. Since the mean free path $\bar{l}$ is a small differential length, the difference in electron concentration can be expressed as

$$n_1 - n_2 = \frac{n(x) - n(x + \Delta x)}{\Delta x} \bar{l}$$  \[3.3.16-1\]
where $x$ is taken at the centre of segment (1) and $\Delta x = \bar{l}$ (see Figure 3.3.16-2)

![Diagram of electron concentration gradient](image)

**Figure 3.3.16-2**  Two segments centred on $x_0$ of an arbitrary electron concentration gradient (Streetman & Banerjee, 2000).

In the limit of small $\Delta x$ (i.e. small $\bar{l}$), the electron flux density can be rewritten in terms of the carrier gradient $dn(x)/dx$

$$\Phi_n(x) = \frac{\bar{l}^2}{2\bar{l}} \lim_{\Delta x \to 0} \frac{n(x) - n(x + \Delta x)}{\Delta x} = \frac{-\bar{l}^2}{2\bar{l}} \frac{dn(x)}{dx} \quad [3.3.16-2]$$

The quantity $\bar{l}^2/2\bar{l}$ is called the *electron diffusion coefficient* $D_n$ (units cm$^2$/s) and the negative simply indicates that the net motion of electrons due to diffusion is in the direction of decreasing electron concentration. The same approach can show that holes in a hole concentration gradient move with a diffusion coefficient $D_p$ (units cm$^2$/s), so that both equations can be written as

**Diffusion of electrons**

$$\Phi_n(x) = -D_n \frac{dn(x)}{dx} \quad [3.3.16-3]$$

and

**Diffusion of holes**

$$\Phi_p(x) = -D_p \frac{dp(x)}{dx} \quad [3.3.16-4]$$

Therefore the current density $J$ expressions are simply
3.3.16-5

\[ J_n(\text{diffusion}) = -(-q)D_n \frac{dn(x)}{dx} = +qD_n \frac{dn(x)}{dx} \]

and

\[ J_p(\text{diffusion}) = -(+q)D_p \frac{dp(x)}{dx} = -qD_p \frac{dp(x)}{dx} \]  

3.3.16-6

With diffusion, electrons and holes move in the same direction in a carrier gradient but the resulting currents are in opposite directions. (Streetman & Banerjee, 2000).

3.3.17 Total Current Density

When a carrier gradient and an electric field are present in a semiconductor, the current densities for electrons and holes will have a diffusion component and a drift component

\[ J_n(x) = q\mu_n n(x)\xi(x) + qD_n \frac{dn(x)}{dx} \]  

3.3.17-1

\[ J_p(x) = q\mu_p p(x)\xi(x) - qD_p \frac{dp(x)}{dx} \]  

3.3.17-2

Therefore, the total current density is the sum of the contributions due to electrons and holes, as is expressed by

\[ J(x) = J_n(x) + J_p(x) \]  

3.3.17-3

3.3.18 The pn-Junction

A p-type semiconductor will have its Fermi level situated somewhere near the valence band and an n-type semiconductor will have its Fermi level situated somewhere near the conduction band as shown in Figure 3.3.18-1.
Both positions of these Fermi levels are dependent on the number of acceptor atoms and donor atoms that are distributed throughout the respective materials as shown by the equations

\[ E_i - E_F = kT \ln \frac{P_0}{n_i} \]  \hspace{1cm} [3.3.18-1]

\[ E_F - E_i = kT \ln \frac{n_0}{n_i} \]  \hspace{1cm} [3.3.18-2]

An epitaxial junction which has a well defined change (abrupt change) from a p-type semiconductor to an n-type semiconductor is called a step junction. If separate, both Fermi levels at equilibrium would be at different positions inside their band gaps but when brought together (i.e. a \textit{pn}-junction) the Fermi level must be constant throughout the device as shown in Figure 3.3.18-1.
Figure 3.3.18-1 The resultant energy band diagram when an abrupt junction is formed between a $p$-type and $n$-type semiconductor.

What process occurs when the two different types of semiconductor are first brought together is as follows. At contact, diffusion of electrons from the $n$-type into the $p$-type and holes from the $p$-type into the $n$-type would immediately take place across the boundary because of the large carrier concentration gradients at the junction. This diffusion process creates a space charge of uncompensated donors ($N_d^-$) in the $n$-type material and an opposite space charge of uncompensated acceptors ($N_a^+$) in the $p$-type material (see Figure 3.3.18-2). These resulting areas of space charge on either side of the junction create an electric field that forces carriers back across the junction. An equilibrium state is reached where the net current created by the diffusion process is countered by the net drift current created by the electric field.

$$J_p^{\text{(drift)}} + J_p^{\text{(diffusion)}} = 0 \quad [3.3.18-3]$$

$$J_n^{\text{(drift)}} + J_n^{\text{(diffusion)}} = 0 \quad [3.3.18-4]$$

The electric field appears in region $W$ (depletion zone) about the junction and there is an equilibrium potential difference $V_0$ across $W$. 
Figure 3.3.18-2 Space charge distribution within the depletion zone with doping concentrations being equal.

By taking the equation $\xi(x) = -\frac{dV(x)}{dx}$ for calculation of an electric field, combining it with equation [3.3.17-1] and then integrating over the appropriate limits, the following equations are derived

$$-\frac{q}{kT} \int_{V_p}^{V_n} \frac{dV}{p} = \int dV \frac{1}{p}$$  \hspace{1cm} [3.3.18-5]

$$-\frac{q}{kT} (V_n - V_p) = \ln p_n - \ln p_p = \ln \frac{p_n}{p_p}$$  \hspace{1cm} [3.3.18-6]

$$V_0 = \frac{kT}{q} \ln \frac{p_p}{p_n}$$  \hspace{1cm} [3.3.18-7]

where $V_0 = V_n - V_p$

This equation can be written as

$$V_0 = \frac{kT}{q} \ln \frac{N_a}{n_i^2/N_d} = \frac{kT}{q} \ln \frac{N_a N_d}{n_i^2}$$  \hspace{1cm} [3.3.18-8]

by considering the majority carrier concentration to be the doping concentration on each side of the contact boundary (i.e. holes in the $p$-type side are majority carriers $p_p = N_a$ and holes in the $n$-type side are minority carriers $p_n = n_i^2 / N_d$).
3.3.19 Space Charge

The space charge width at the boundary of a pn-junction is determined by the doping concentrations in the p-type and n-type semiconductor. Specifically, it is the lower doping concentration side that produces the majority of the resulting space charge as shown in Figure 3.3.19-1.

By ignoring carriers within the space charge region, the positive charge density on the n side of the boundary is equal to the concentration of donor ions $N_d$ times $q$ while the negative charge density on the p side is equal to the concentration of acceptor ions $N_a$ times $q$ and is expressed as $Q_+ = |Q_-|$. When examining a sample of cross sectional area $A$, the total uncompensated charge on either side of the junction is

$$qAx_{p0}N_a = qAx_{n0}N_d \quad [3.3.19-1]$$

which reduces to

$$x_{p0}N_a = x_{n0}N_d \quad [3.3.19-2]$$

where $x_{p0}$ is the penetration of the space charge region into the p-type material, $x_{n0}$ is the penetration of the space charge region into the n-type material and $x_{p0} + x_{n0} = W$. For both sides to be equal when doping concentrations are different, the distance of the space
charge into the material must vary accordingly. When one side of the junction has a much higher doping concentration than the other side (i.e. \( N_d > N_a \)), the space charge region on that side can be considered as occurring approximately at the boundary since \( x_{p0} \approx x_{n0} \).

Following from this, the majority of the space charge region must penetrate into the lower doping concentration side.

3.4 Cadmium Sulphide and the Heterojunction

With a simple pn-junction, one side of the junction is doped as n-type while the other side is doped as p-type and the base material for both sides of the junction is the same. With other junction designs, the base material does not have to be the same on both sides of the junction to create the depletion later and associated space charge. These types of junctions, where the base material on one side is different to the other side are called heterojunctions. Solar cells and infrared imaging detectors are good examples of heterojunctions.

To produce n-type CdS thin films for use in solar cells is a simple process, the current preferred method being CVD whilst CBD has also shown excellent potential. The most common doping material is the element Indium (In) which is easily introduced into the CBD process (at very low concentrations), to produce n-type CdS thin films.

3.5 Theory of CBD

With solution deposition techniques, there are a number of chemical and physical parameters which define the growth mechanism. They include relative concentrations of precursors, solution pH values, the use of buffers, temperature and solution mixing. With CBD CdS thin films the scientific literature indicates that the film morphology consists of a continuous (monolayer growth) and a particulate phase (nucleation growth). If the continuous phase dominates the process, then the films optical characteristics are excellent (type A). But if the particulate phase dominates the process, then very poor quality thin
films are the result (type B). Studies of the growth process of CBD CdS thin films have shown that film growth occurs by an ion-by-ion condensation of the impinging particles ($Cd^{2+}$ & $S^{2-}$) and by colloidal particles of CdS adhering to the substrate surface. The colloidal particles grow in size with time, forming the particulate part of the film (Sebastian & Hu, 1994).

3.5.1 CBD CdS Chemistry

By using different chemical solutions that contain cadmium and sulphur ions separately, a number of alternative schemes are possible for the formation of CdS thin films. These CdS thin films can be prepared by the decomposition of thiourea (or thioacetamide) in an alkaline solution of cadmium salts according to the following reaction (for cadmium acetate salt):

\[
Cd(CH_3COO)_2(aq) + (NH_2)_2CS(aq) + 2OH^- \rightarrow CdS(s) + H_2CN_2(aq) + 2H_2O + 2CH_3COO^-(aq)
\]  
[3.5-1]

where the salt can also be $CdSO_4$, $Cd(NO_3)_2$, or $CdCl_2$.

This overall reaction can be displayed in parts for a better understanding of the reactions taking place.

1. Cadmium disassociates and combines with the hydroxide to form insoluble cadmium hydroxide.

   \[
   Cd^{2+} + 2OH^- \rightleftharpoons Cd(OH)_2
   \]  
[3.5-2]

2. The thiourea readily reacts with the hydroxide ions to form the sulphur ions.

   \[
   CS(NH_2)_2 + 2OH^- \rightarrow S^{2-} + CH_2N_2 + 2H_2O
   \]  
[3.5-3]

3. Cadmium ions are released by decomplexation

   \[
   Cd(NH_3)^{2-} \rightleftharpoons Cd^{2+} + 4NH_3
   \]  
[3.5-4]

4. Cadmium ion combining with the sulphur ion by displacing the hydroxide ion
For \( \text{CdS} \) to form on the surface of a substrate requires that either the \( \text{Cd}^{2+} \) or the \( \text{S}^{2-} \) are initially bonded to the substrate surface. But preferential absorption of either precursors on glass surfaces is unknown and so for \( \text{CdS} \) to form on the glass substrate, requires some form of catalyst action. This is achieved by the \( \text{Cd(OH)}_2 \) suspension which is known to activate the decomposition of thiourea as shown by expression [3.5-3]. The \( \text{Cd(OH)}_2 \) suspension has an attraction to substrate surfaces via its \( \text{OH}^- \) ligand because glass surfaces are hydrophilic surfaces, which preferentially absorb \( \text{OH}^- \) ions. So \( \text{CdS} \) deposition is directly related to the \( \text{Cd(OH)}_2 \) in solution and when this \( \text{Cd(OH)}_2 \) is present as a fine dispersion, it absorbs preferentially on solid substrate surfaces, catalyzing the decomposition of thiourea to form \( \text{CdS} \) (Kaur, Pandya & Chopra, 1980).

### 3.5.2 Growth Kinetics

By manipulating the equilibrium conditions [3.5-6] and [3.5-7] in order to produce a graphical solution to these equations as shown in Figure 3.5-1, enables the identification of optimum conditions for type A and type B thin film growth (Gluszak, 1996; Kaur, Pandya & Chopra, 1980).

\[
\text{Cd(OH)}_2 \leftrightarrow \text{Cd}^{2+} + 2\text{OH}^-
\]  

[3.5-6]

\[
\text{Cd(NH}_3)_4^{2+} \leftrightarrow \text{Cd}^{2+} + 4\text{NH}_3
\]  

[3.5-7]

Taking equation [3.5-6] and expressing its solubility product (SP) to obtain

\[
\text{SP} = [\text{Cd}^{2+} ][\text{OH}^-]^2
\]  

[3.5-8]

Taking equation [3.5-7] and expressing the instability constant \( (K_i) \) for cadmium tetrammine to obtain
\[
K_i = \frac{[Cd^{2+}][OH^-]^2}{[Cd(NH_3)_4^{2+}]} \quad [3.5-9]
\]

where the square brackets \([\phantom{0}]\) refer to concentrations at equilibrium.

Taking the logarithm of equations [3.5-8] and [3.5-9], changing to concentration exponents and solving for pH to obtain

\[
pH = \frac{1}{2} p[Cd] - \frac{1}{2} p[SP] + p[K_w] \quad \text{where } K_w = 10^{-14} \text{ for water.} \quad [3.5-10]
\]

and

\[
4p[NH_3] = p[K_i] + p[Cd(NH_3)_4^{2+} - p[Cd^{2+}] \quad [3.5-11]
\]

The equation [3.5-10] is acceptable for graphing but equation [3.5-11] needs to be modified before it can be used. The \(p[NH_3]\) term in equation [3.5-11] needs to be transformed into something more useful and this is achieved by using the reaction equation [3.5-12] for ammonia in aqueous solutions

\[
NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^- \quad [3.5-12]
\]

and the ionization constant of ammonium hydroxide \((K_b^*)\) to form equation [3.5-13].

\[
K_b^* = \frac{[NH_4^+][OH^-]}{[NH_3]} \approx \frac{[OH^-]^2}{[NH_3]} \quad [3.5-13]
\]

By taking the logarithm of equation [3.5-13], the equation [3.5-14] is obtained

\[
pK_b^* = 2p[OH^-] - p[NH_3] \quad [3.5-14]
\]

and by using the identity \(p[K_w] = pH + p[OH^-]\) to substitute for the hydroxide and rearranging, the equation becomes

\[
\]

Substituting equation [3.5-15] into [3.5-11] results in the equation

\[
pH = p[K_w] - \frac{1}{2} p[K_i] - \frac{1}{2} p[K_b^*] - \frac{1}{6} p[Cd(NH_3)_4^{2+}] + \frac{1}{6} p[Cd^{2+}] \quad [3.5-16]
\]
To be able to use equation [3.5-16] the assumption is made that the concentration of $NH_3$ is in excess which allows the use of the approximation $[Cd(NH_3)_4^{2+}] = [Cd(CH_3COO)_2]$, the concentration of the salt being a known quantity.

Equations [3.5-10] and [3.5-16] are called the Hydroxide line and Complex line respectively. The equations produce a plot as shown in Figure 3.5-1 when pH is plotted against $[Cd^{2+}]$.

**Hydroxide Line**

$$pH = \frac{1}{2}p[Cd] - \frac{1}{2}p[SP] + p[K_w]$$  \hspace{1cm} [3.5-10]

**Complex Line**

$$pH = p[k_w] - \frac{1}{6}p[K_1] - \frac{1}{2}p[K_b^*] - \frac{1}{6}p[Cd(NH_3)_4^{2+}] + \frac{1}{6}p[Cd^{2+}]$$ \hspace{1cm} [3.5-16]

---

**Figure 3.5-1** A graph of pH verses $[Cd^{2+}]$ showing areas of optimal CdS thin film formation.
The graph displayed in Figure 3.5-1 shows the hydroxide line and the complex line crossing over and where this crossover occurs a vertical dashed line has been drawn with labeling of Region I and Region II for depicting the left side and right side respectively. This graph shows that $Cd(OH)_2$ is formed in solution only for pH values above the hydroxide line. It also shows that the complex $Cd(NH_3)_2^{2+}$ is stable for pH values below the complex line but is hydrolyzed to $Cd(OH)_2$ above the complex line. In region I, the area between the hydroxide line and complex line (shaded gray) is where equilibrium conditions exist and where $Cd(OH)_2$ plus $Cd(NH_3)_2^{2+}$ coexist in solution. Thus type A films are formed in this section but only when a very small amount of $Cd(OH)_2$ is in the solution. Using large amounts of $Cd(OH)_2$ leads to precipitation only and not film formation.

In region II, the hydroxide line lies above the complex line so for any $Cd(OH)_2$ to be formed at all requires the physical introduction of a hydroxide. Thus type A films can also be formed in region II, just above the hydroxide line (shaded patchy gray), with the addition of hydroxide to the solution. Care must be taken because with too much hydroxide added, the reaction rate is so high that precipitation of $CdS$ results.

In region II, below the hydroxide line there is no $Cd(OH)_2$ available to assist in the $CdS$ deposition and this results in the formation of type B films. Type A films can only be obtained from this section by increasing the deposition solution temperature in conjunction with vigorous mixing. The increase in temperature causes the $CdS$ ionic product to be greater than its solubility product while also increasing the decomposition of thiourea. The vigorous mixing provides kinetic energy to the ions resulting in an increased number of collisions to form $CdS$. (Kaur, Pandya & Chopra, 1980).
3.6 Theory of Analytical Experiments

The CdS thin films created by both groups were subjected to six different analytical experiments (PIXE, RBS, AFM, XRD, and XPS) in order to extract a broad range of information about the growth processes involved. Each analytical experiment obtains information from these thin films by a different method so that the composite picture of the CdS thin film growth processes is much clearer.

3.6.1 Particle Induced X-ray Emission (PIXE).

PIXE is based upon the excitation of the inner most electrons of the atom by energetic protons. Bombardment with ions of high enough kinetic energy (usually MeV protons \( ^1H^+ \)) produced by an ion accelerator, will cause inner K shell and L shell ionization of atoms in the near surface (10 \( \mu \)m) of a material target. Outer shell electrons drop down to replace inner shell vacancies caused by this ionisation, though only certain transitions are allowed. X-rays of a characteristic energy of the element are emitted and an x-ray energy detector is used to record and measure the resulting energy spectrum. The x-rays are sorted by energy and are counted which allows the identification of atoms and the concentrations. Because PIXE spectra can be complex when doing multielement analysis, computers are usually used to deconvolute the spectrum and resolve the components. Before an analysis run begins the analysis instrumentation must be calibrated against known elements or compounds of high purity. The actual analysis run is then performed with the instrument settings unchanged.

When a proton ion having a few MeV kinetic energy is allowed to interact with atoms in a target sample, collisions will occur usually with the electrons having a high effective cross-sectional area (probability that an event will occur) in the target atoms. The cross-sections for different shells are very different and are a complex function of proton velocity, and target atomic number. For target atoms of low atomic number K-shell
ionization dominates, but as atomic number of the target atoms increases the L-shell ionizations tend to become more prevalent.

Compared to electron based x-ray analytical techniques, PIXE offers better peak to noise ratios and consequently much higher trace element sensitivities. High trace sensitivity to a given trace element is dependent upon a number of factors, such as matrix composition of the target, detector type, detector energy efficiency, x-ray filter attenuation, detector window attenuation and x-ray energy peak overlap. Because lower energy X-rays tend to be attenuated much more than higher energy X-rays as shown in Figure 3.6.1-1, allowances for these differences must be made.

![Graph of efficiency verses energy for different parts of PIXE instrumentation.](image)
3.6.2 Rutherford Backscattering (RBS)

Rutherford backscattering spectrometry is a high energy ion beam technique primarily applied to measure elemental composition (stoichiometry) or impurity concentration as a function of depth in the near-surface region of a solid. It is a fast, quantitative, matrix independent, usually non-destructive method that does not require standardisation and has approximately 1% to 3% accuracy. The typical experimental arrangement requires laterally uniform samples (flat) of millimetre-size dimensions and employs 1 to 3 MeV $^4$He$^{++}$ ions to achieve depth resolutions between 50 and 300 Å and accessible depths up to a few micrometres.

Mass resolution for the lighter elements is generally good but significantly deteriorates for the heavier elements. Thus, other detection methods should be used for these heavier elements for positive identification, such as PIXE analysis which shares the same instrumentation as the RBS system, but uses an X-ray detector.

Normally, RBS is associated with the analysis of amorphous materials but if crystalline materials are analysed, then special effects (called channeling) can occur which can yield information about the sample structure or lattice location of impurities.

An RBS measurement consist of irradiating a sample with high-energy (MeV) light ions and measuring the energy distribution of the ions that are backscattered through a particular large angle as shown in Figure 3.6.2-1. The scattering is due to the Coulomb repulsion of the projectile ion from the target nucleus, the angle $\theta$ between the incident beam direction and the direction of the deflected particle is called the scattering angle. (Börgesen, 1991).
Normally detectors are positioned at one or more scattering angles to count the particles scattered into the small cones of solid angle subtended by the detector. For Coulomb scattering between a positively charged particle and a positively charged nucleus, the trajectories will resemble those shown in Figure 3.6.2-2. When the impact parameter $b$ is small, the distance of closest approach $r_{\text{min}}$ is small (particles 1 & 2) and the Coulomb force is large. A large Coulomb force will produce a large scattering angle and the particle can be repelled backwards. Conversely, for large impact parameters the particles never get close together, so the Coulomb force is small and the scattering angle is also small (particles 3 & 4).
The derived relationship between $b$ and $\theta$ is

$$b = \frac{Z_1 Z_2 e^2}{8\pi \varepsilon_0 K} \cot \frac{\theta}{2}$$

[3.6.2-1]

where $K = m v_0^2 / 2$, $Z$ equals the atomic number of the incident particle or scatterer, $e = 1.6 \times 10^{-19} \text{C}$ and $\varepsilon_0 = 8.85 \times 10^{-12} \text{F/m}$.

To derive this relationship, the following assumptions are made:

I. The scatterer is so massive that it does not significantly recoil; therefore the initial and final kinetic energies of the $\alpha$ particle are practically equal.

II. The target is so thin that only a single scattering event occurs.

III. The bombarding particle and target scatterer are so small that they may be treated as point charges.

IV. Only the Coulomb force is effective.

Thornton & Rex, 1993, p.145)

Because in an experiment it is impossible to select individual impact parameters, when a detector is placed at a particular angle $\theta$, an actual finite $\Delta \theta$ is covered which corresponds to a range of impact parameters $\Delta b$. Now the probability of a particle being scattered is equal to the total target area exposed for all the nuclei divided by the total target area $A$. If $\sigma$ is the cross section for each nucleus and $n_t$ equals the number of scattering nuclei per unit area, then $n_t A \sigma$ is the total area exposed by the target nuclei and the fraction of incident particles scattered by an angle of $\theta$ or greater is

$$f = \frac{\text{Target area exposed by scatterers}}{\text{Total target area}} = \frac{n_t A \sigma}{A} = n_t \sigma = n_t b^2$$

[3.6.2-2]

$$f = \pi n_t \left( \frac{Z_1 Z_2 e^2}{8\pi \varepsilon_0 K} \right)^2 \cot^2 \frac{\theta}{2}$$

[3.6.2-3]
In an actual experiment, a detector is positioned only over a range of angle $\theta$, $\theta$ to $\theta + \Delta \theta$, as shown in Figure 3.6.2-3.

Figure 3.6.2-3 Range of scattering angle that the detector head encompasses.

(Thornton & Rex, 1993)

Therefor, there is the need to know the number of particles scattered between $\theta$ to $\theta + \Delta \theta$ that corresponds to incident particles with impact parameters between $b$ to $b + db$ as shown in Figure 3.6.2-4.

Figure 3.6.2-4 Particles over the range of impact parameters from $b$ to $b + db$ will scatter into the angular range $\theta$ to $\theta + d\theta$ (Thornton & Rex, 1993).
As shown by Figure 3.6.2-4, the fraction of incident particles scattered between \( \theta \) to \( \theta + \Delta\theta \) is \( \frac{df}{d\theta} \) and is found by taking the derivative of equation [3.6.2-3].

\[
\frac{df}{d\theta} = -\pi nt \left( \frac{Z_1 Z_2 e^2}{8 \pi e_o K} \right)^2 \cot^2 \frac{\theta}{2} \csc^2 \frac{\theta}{2}
\]  

[3.6.2-4]

Therefore, the number of particles scattered per unit area, \( N(\theta) \), into the ring at scattering angle \( \theta \) is

\[
N(\theta) = \frac{N_t |df|}{dA} = \frac{N_{nt}}{16} \left( \frac{e^2}{4 \pi e_o} \right)^2 \frac{Z_1^2 Z_2^2}{r^2 K^2 \sin^4 (\theta/2)}
\]

[3.6.2-5]

where \( N_t \) equals the total number of incident particles.

The important points of this equation, called the Rutherford scattering equation, are

I. The scattering is proportional to the square of the atomic number of both the incident particle \( (Z_i) \) and the target scatterer \( (Z_2) \).

II. The number of scattered particles is inversely proportional to the square of kinetic energy \( K \) of the incident particle.

III. The scattering is inversely proportional to the fourth power of \( \sin (\theta/2) \) where \( \theta \) is the scattering angle.

IV. The scattering is proportional to the target thickness for thin targets.

(Thornton & Rex, 1993, p.144-152)

The RBS spectrum is relatively easy to interpret, it being basically shaped by two processes, the energy lost by the high-energy ion in traversing into and out of the sample and the energy lost due to the backscatter from the target atom. These two processes depend on the number of atoms per unit area (areal density) that are encountered and not
the density of the material. Quantified data against standards is available so the only unknown is the composition of the sample. An exact interpretation of the signal heights in an RBS spectrum generally requires the use of tailored software.

There are some limitations which can detract from the accuracy of the Rutherford scattering equation and they are: multiple scattering, energy straggling, material is smaller than the beam size, required absolute cross sections, increasing cross sections at higher energies, plural medium angle scattering resulting in backscattering, rough surfaces at the atomic scale and most solids tend to exhibit one or more preferential directions.

3.6.3 Atomic Force Microscopy (AFM)

In AFM, a Silicon Nitride tip ($Si_3N_4$) is mounted on a cantilever having a very small force constant. This results in the cantilever being deflected when a sample is scanned along the tip. The AFM can be operated in the attractive regime or repulsive regime, and can be used to measure atomic (van der Waals) forces, electrostatic forces or magnetic forces. Deflections of the cantilever are usually detected with an optical interferometer or direct reflection of a laser beam.

A major problem with these systems is the uncontrolled motion of the electrodes caused by vibration, resonance and thermal drift. With effective systems, combining high stiffness and good vibration isolation, vibration amplitudes as low as 10 pm can be obtained.

Data is in the form of an image or graphical representation of the surface which can be used for estimations of grain sizes, grain shapes and thickness of films (after etching).

3.6.4 Grazing Incidence Diffraction (XRD)

X-ray diffraction methods are widely used for the characterisation of materials. The increasing use of thin films with special tailored properties for electronic devices has resulted in the grazing incidence diffraction method being specifically devised for
characterisation of these thin films. In the usual XRD setup the coupling between the specimen surface and the detector is maintained at a $\theta : 2\theta$ angular relation (ratio) but with grazing incidence diffraction the sample surface is kept fixed (see Figure 3.6.4-1) in relation to the incident x-ray beam and only the detector is moved (called $2\theta$).

![Diagram showing moveable x-ray detector and fixed position of sample.](image)

Figure 3.6.4-1 Simplified diagram showing moveable x-ray detector and fixed position of sample.

The specimen can be set at any desired angle and the pattern recorded by $2\theta$ step scanning. Thus reflections take place only from planes inclined to the surface (see Figure 3.6.4-2), the angle between the Bragg plane and the surface is $\theta - \alpha$ where $\alpha$ is the grazing incidence angle.
The depth of x-ray penetration into the thin film depends on the angle of incidence $\alpha$ and the formula for the critical angle of incidence for total reflection $\alpha_c$ from a plane within the film is

$$\alpha_c = \left(2\delta\right)^{1/2} = 1.6 \times 10^{-3} \rho \lambda$$ \[3.6.4-1\]

where $\alpha_c$ is in radians, $\rho$ is the density in g/cm$^3$ and $\lambda$ is the x-ray wavelength in Å.

When $\alpha < \alpha_c$, the penetration depth $t'$ is determined by calculating the total external reflection process and is expressed by the formula

$$t' = \frac{\lambda}{\left[2\pi \left(\alpha_c^2 - \alpha^2 \right)^{1/2}\right]}$$ \[3.6.4-2\]

$$t' = \frac{\lambda}{\left[2\pi \left(2.56 \times 10^{-6} \rho \lambda^2 - \alpha^2 \right)^{1/2}\right]}$$ \[3.6.4-3\]

When $\alpha > \alpha_c$ the penetration depth is dependent on the linear absorption coefficient $u_i$

$$t' = \frac{2\alpha}{u_i}$$ \[3.6.4-4\]

The advantage of grazing incidence diffraction is most of the information is derived from the actual thin film and not the substrate.

The disadvantage is that the detector scan times are greatly extended in order to obtain good information (a reduction of about 90% in intensity from the usual XRD), thus the thinner the film the longer the required run time. Also, the obtained spectrum is shifted
slightly to higher angles than those calculated from the Bragg Law \(2d \sin \theta = n\lambda\) and must be taken into account when determining the lattice spacings. The reason for this \(\Delta 2\theta\) shift is that the index of refraction of x-rays is slightly less than unity, being calculated as 

\[n = 1 - \delta\]

where \(\delta\) is approximately equal to

\[\delta = 1.28 \times 10^{-6} (p\lambda)^2\]  \[3.6.4-5\]

Today sophisticated software packages take this \(\Delta 2\theta\) shift into account for grazing incidence diffraction spectrums.

Multiple runs are needed to build up a good statistical count of x-rays over the required range of angles, especially as grazing incidence diffraction only produces about 10% of the normal x-ray diffraction count rate.

3.6.5 Electron Spectroscopy for Chemical Analysis (ESCA)

ESCA is also commonly called X-ray Photoelectron Spectroscopy (XPS) and is a non-destructive surface analysis technique using one of the most fundamental interactions of photons with matter, the photoelectric effect. The sample is kept in a very high vacuum and bombarded with x-ray photons from an x-ray tube (see Figure 3.6.5-1), the photons having sufficiently high enough energy \((E = h\nu)\) to be absorbed by the inner shell electrons. This absorption of the energy by the electron results in its physical ejection (photoelectron) from the atom with kinetic energy \(E_k\). If after ejection, no collisions take place within the material, the electrons kinetic energy will be conserved when it leaves the material. This kinetic energy can be measured to a high degree of precision using an electrostatic analyser.
The photon penetration is relatively large in solid materials (a few micrometres for kilo-electron (keV) x-rays) but the photoelectrons used for analysis only come from the superficial layers and this is because any photoelectrons coming from deeper layers suffer inelastic collisions in the material. The universal electron mean free path curve for photoelectrons with kinetic energies from 0 to 1500 eV, shows that an electron in a material might only travel 3 to 30 Å before suffering an inelastic collision (see Figure 3.6.5-2).
Figure 3.6.5-2 Graph of Electron mean free path verses Electron kinetic energy.

This curve is not particularly material dependent and is well described by the formula $\lambda \approx E^{0.75}$ for values of 30 eV's and above. Because the electrons detected in the photoelectron peaks come from an average depth of about 30 angstroms below the surface the photoelectron spectroscopy method is only sensitive to the extreme surface of the material.

If the photoelectron analyser is rotated so that the analysed electrons originate from an almost grazing ejection angle relative to the surface of the material, then the useful electron escape depth is reduced by a sine function. The effect is that the surface sensitivity is increased and the photoelectrons originate from a much shallower depth.

The XPS detection limit is in the range of 0.1 to 1% in the number of atoms and is due to variations of the photoelectric cross-sections and the electron mean free paths. A sample surface would typically contain $10^{15}$ of atoms per cm$^2$ and so the detection limit is $10^{12}$ to $10^{13}$ atoms on the surface. Since the bulk of a solid contains $10^{20}$ atoms per cm$^3$, the XPS method is able to detect on the surface of the material segregated elements in the range of
$10^{-3}$ to $10^{-7}$ compared to the bulk (ie. 0.01 to 0.1 part per million (p.p.m.)). (Pireaux & Sporken, 1991)

The surface sensitivity is one great advantage of the XPS method, being able to give elemental and chemical composition of the outermost atomic layers of a material. But a disadvantage would have to be that the method is extremely sensitive to surface contamination and thus great care must be taken when handling samples. That is why the XPS method requires a very high vacuum ($<10^{-9}$ torr), so that over the course of one spectra recording (approximately 15 minutes) a reactive surface under investigation is free from any contaminant.

Another feature of XPS is the possibility of identifying the different chemical states of the atoms by observing energy shifts in core electron lines and comparing this information with known database information for identification. (Pireaux & Sporken, 1991)

Qualitative estimation of the types of atoms present at the surface of a sample is possible as long as their relative concentration is at least in the range of 1% at the surface. If the particular photoelectron transmission function of the spectrometer is known then quantification of this information with good accuracy (a few percent) is possible. Given that a measured XPS intensity is proportional to the atomic density, the photoelectron cross-section and the energy transmission function of the analyser

$$I_A = [A] \sigma_A \lambda_A$$

atomic concentrations can easily be derived from the formula

$$\frac{[A]}{[B]} = \frac{I_A \sigma_A^* \lambda_A}{I_B \sigma_B \lambda_B}$$

where $A$ and $B$ refer to two different elements ($B$ is the reference in this case), the square brackets "[ ]" denotes the calculated atomic concentration, $I$ is the measured photoelectric peak intensity or area, $\sigma^*$ is the elemental sensitivity factor for this element (photoelectric
cross-section) modulated by the transmission function $T$ of the spectrometer used to record the spectrum and $\lambda$ is the corresponding photoelectron mean free path. (Pireaux & Sporken, 1991)

Computerised data processing is a very significant step in the analysis of XPS data, the most critical steps being smoothing and filtering for improvement of signal-to-noise ratio of raw data; background and satellite removal for removal of non-essential information; deconvolution (ie. fast Fourier function (FFT)) for yielding the true spectrum (possible only if measured data and the response function are known); differentiation for core-level studies; curve fitting for precise determination of parameters (peak position, intensity and width) of all the peaks contributing to a core-level spectrum; area determination by removal of the background.
Chapter 4 Materials and Methods

This chapter describes all the procedures required for doing the CBD experiment as well as the procedures for analysis of the CdS thin films. See Appendix I for a complete listing of all materials and equipment used.

4.1 CBD Apparatus

The CBD setup used in the creation of the CdS films is shown in Figure 4.1-1. For every experimental run a batch of six slides was produced, showing successive deposition phases, as the experiment proceeds.

Temperature control of the CBD solution was achieved by placing the CBD bowl into a cooling bath of water. The temperature of the cooling bath was kept constant by placing
it onto a Electrothermal electric heater (concave top) that was controlled by a BTC-2200 Fuzzy Logic microprocessor controller using a platinum (Pt) thermocouple temperature sensor. The platinum sensor was protected by placing it in a plastic tube which was scaled at the cooling bowl end.

The solution was stirred using a mixer (propeller shape) which was attached to a long shaft and which in turn was attached to a Universal Electric Co. electric motor. The speed of the motor and hence the mixing speed, was controlled by a Casablanca motor speed control unit.

The glass slides were attached inside the deposition bowl by simply pegging them against the spacers. The spacers are pieces of plastic that have been glued on the inside of the deposition bowl with silicon sealant.

4.1.1 Substrate Preparation

The boro-silicate glass slides that the CdS thin films deposited on were cleaned in order to remove all traces of dirt, oil and grime. The cleaning method was a simple and economical one, the concentrated sulfuric acid being used for numerous cleaning’s. The glass slides were first washed by hand with any commercial solution soap and rinsed properly with Milli-Q water. The slides were then left overnight in a concentrated sulfuric acid bath. The following morning the slides were carefully removed from acid bath and washed in Milli-Q water, after which they were placed into the deposition bowl, using plastic pegs to hold them in place.

4.1.2 Solution Preparation

The deposition bowl final solution volume was 290 ml which allowed the experiment to proceed without any precursor constraints and at the same time, minimized waste disposal problems. The thiourea and cadmium were initially in solid form so solutions at the correct concentrations had to be produced. Also the ammonia solution was highly
concentrated and had to be diluted down to the required molarity. Approximately 230 ml of ammonia solution, a 40 ml cadmium solution and a 20 ml thiourea solution were made up for each experiment and then added together in the deposition bowl, which resulted in a final 290 ml solution volume. This solution had the concentrations of [1.8] M ammonia, [0.004] M cadmium and [0.008] M thiourea. Slight variations in the cadmium and thiourea were used in order to achieve the best possible deposition of CdS thin films.

4.1.3 Procedure

The 6 slides were placed in the deposition bowl with the ammonia solution. The deposition bowl was then placed into the cooling bowl, which was then placed onto the Electrothermal electric heater. Water was then placed into the cooling bowl and the equipment turned on. The temperature quickly reached 60°C and was held constant by the BTC-2200 Fuzzy Logic microprocessor controller. At this point, the 40 ml cadmium solution was added which sometimes caused a slight temperature drop. When the temperature had stabilised at 60°C, the thiourea was added and the timer started. After 20 to 30 minutes, a very light yellowish film became apparent on the slides. Slides were then removed from the deposition solution at 10 minute intervals, to give a convenient set of films as a function of deposition time. Each slide was washed with Milli-Q water and then placed into the ultrasonic cleaner containing Milli-Q water for about 10 minutes. After cleaning, the slides were air dried and placed into resealable plastic bags to minimise contamination. In its simplest form, 0.004 M concentration of cadmium acetate (Cd$^{2+}$) and 0.008 M concentration of thiourea (S$^{2-}$) are added to a 1.8 M concentration of ammonia solution (NH$_3$). This final solution is kept at a constant 60°C and continuously mixed to achieve even precursor density distributions throughout the solution. Immersed in the deposition solution is the thoroughly cleaned glass slides that the CdS films will form on.
4.1.4 Post Deposition Treatment

The only post treatment of the CdS thin films was to remove small sections of the thin film from the slides in order to do direct depth profiling using the AFM instrumentation. Initially concentrated sulphuric acid was used to remove the films though problems were encountered with this method. The two different masks employed to allow the acid to create a step in the film did not function properly. A sharp transition from film to glass substrate was needed simply because when using the AFM instrumentation, the maximum possible x or y direction cantilever travel was 10 μm. Eventually a solution was found for group B slides by simply and gently scribing a line with a smooth blunt screw driver. For group A slides this method failed, as the films was very tough and adhered strongly to the glass substrate surface. Instead, a wire saw was used to cut down to the glass surface. Dilute sulphuric acid was brushed on to the wire to aid in breaking up the hard CdS film.

4.2 Health and Occupational Safety

Concentrated sulphuric acid and cadmium compounds must be handled carefully. Therefore the use of rubber gloves, fume hoods, breathing protection, laboratory coats and proper waste disposal was necessary. The concentrated acid was always diluted by pouring the acid into water slowly and not visa versa.

In order to minimize waste disposal, the solutions used in the CBD experiment were minimal volumes. After each experiment, the deposition bowl, mixer and shaft were cleaned with minimal quantities of concentrated sulfuric acid. The concentrated acid was reused for the same purpose a number of times before it was also treated as hazardous waste. All used hazardous solutions were kept in a two litre flask which was slowly heated, using a controllable electric heater, in a fume hood. This controlled heating reduced the water volume slowly and made the waste more manageable for proper disposal.
4.3 Analysis Facilities and Instruments

To investigate what is occurring at the surface of the slides during deposition, this project used six different analysis techniques as well as a number of different software packages to manipulate obtained data. Each analysis technique can investigate a different aspect of the films forming on the surface of the slides so that a description of what is happening during deposition can be formed. Details of each analysis technique, facilities and software packages used are further discussed in the following sections.

4.3.1 PIXE experiment

PIXE measurements were performed using the 3 MV Multiple Surface Analysis Facility (SR2) at ANSTO, Lucas Heights, Sydney (see Figure 4.3.1-1). The particle beam consisted of 2.5 MeV proton $^1H^+$ ions at a beam current of approximately 10 nano amperes and the detector angle was $135^\circ$. Before doing the analysis run, calibration was first done against elemental compound standards with very accurate concentrations. A high accuracy for sulphur was achieved but for cadmium there was a problem as no suitable reference compound was available. Calibration against reference standards resulted in an accuracy of 1% for sulphur and 8% for the cadmium.

Using tape, the CdS deposited glass slides were secured onto a multiple sample feed system, approximately 20 samples per analysis run. A total of 80 samples were tested by the facility over a period of two days.
Figure 4.3.1-1 Schematic of PIXE instrumentation.

In-house software was used for element identification, concentration calculations and graphical file production. Element identification could also be achieved by simply identifying a peak energy position and checking this energy against an "X-Ray Emission Lines" table as shown in Appendix II. Microsoft Excel software was used to create tables with columns labeled as "element concentration", "background" and "error" for a number of identified elements. Microsoft Excel software was also used for further information processing as well as additional graphical file production.

4.3.2 RBS experiment

RBS measurements were performed using the 3 MV Multiple Surface Facility (SR2) at ANSTO, Lucas Heights, Sydney (see Figure 4.3.2-1). The particle beam consisted of 2.5 MeV proton $^1H^+$ ions and the detector angle was 169°. RBS analysis and PIXE analysis share the same instrumentation, the only difference being the detectors. So using
tape to secure the glass slides, approximately 20 samples per analysis run were loaded onto
the multiple sample feeder and a total of 27 samples were tested by the facility.

RUMP software was used for analysing data and producing graphical plots. The simulation
feature of the RUMP software was used to compute the expected spectrum for the CdS
samples. This synthesized spectrum was then directly compared against the actually
measured spectrum for any differences. This feature enabled fast identification of bulk CdS
material as well as identification of different glass types used in the experiments.

4.3.3 AFM experiment

AFM measurements were performed using a Digital Instruments NanoScope IIIa at
the School of Applied Chemistry, AFM laboratory, Curtin University of Technology, Perth
(see Figure 4.3.3-1).

Figure 4.3.2-1 Schematic of RBS instrumentation
Digital Instruments proprietary software was used for analysis of information as well as production of the topological and side-view graphical images. A number of slides were etched by various means to obtain depth profiling information from the AFM analysis. Calculations of film thickness was possible from the software package, but the software calculated thickness was either accepted or rejected after physically drawing lines of best fit on the side-view images and measuring the thickness. The graphical side-view shown in the top left hand corner of Figure 4.3.3-2 is one of the best obtained and the vertical heights calculated by the software can be accepted by simply averaging the three heights.
Figure 4.3.3-2 A example of the Digital Instruments NanoScope 111 a software calculations and graphical output.

The top-down image and the side-view image show that this particular scanned area of the CdS slide is slanting up towards the viewer and is typical of all the slides investigated, that different areas on a slide exhibit slants in different directions.

4.3.4 XRD experiment

XRD measurements were performed using a Siemens D5000 Grazing Incidence Diffractometer at the Department of Applied Physics, Curtin University of Technology. The x-ray tube voltage was set at 40 KV and a tube current of 20 milli amps. The angle range examined was from 20° to 70° in 0.02° step increments. The angle of incidence for the x-ray beam was set to 3° to enable a good overall spectrum from the entire thin film.
For each sample, the detector scan process took approximately 24 hours to obtain a good spectra with minimal background noise.

Figure 4.3.4-1 A photograph of a Siemens D5000 Grazing Incidence Diffractometer.

The resulting 2θ XRD spectrum was analysed with the software package MDI Jade 5.0. The software smoothed and filtered the obtained spectra while identification of peaks was made using the appropriate materials database.

4.3.5 ESCA experiment

ESCA measurements were performed using an Kratos Axis Ultra Scanning ESCA system, at the Surface Analysis Laboratories, Murdoch University (see photo 4.3.5-1). An unfiltered Al Kα (1486.6 eV) radiation source was used for the survey (entire range) scans while a monochromator was additionally used for the high resolution scans.
Kratos propriety software was used for identification of elements and the production of graphical plots. In-house software was used for merging data and XPSpeak 4.1 (Kwok, 1999) software was also used for producing graphical plots.
Chapter 5  Results / Analysis

In this chapter is presented the data from all the analysis experiments performed on the CdS thin films. This data is inspected, explained and manipulated in order to extract relevant information about the growth process of CdS thin films.

5.1  Visual Inspection

First impressions of the CdS thin films from both groups was that they looked and behaved the same, though this was soon dispelled with some rudimentary analysis. Group A films were much harder and adhered extremely well to the glass substrate, it being very difficult to scratch the film. These films also had a specular look about them. On the other hand, group B's films were softer and it was very easy to scratch the film off the substrate with moderate pressure. These films were more opaque in colour than group A's films and exhibited a slight powdery look. Further analysis confirmed that these CdS thin films from the two groups were very different.

5.2  PIXE analysis

With the PIXE analysis, a series of spectra graphs for each experiment were obtained (one spectra produced from each slide) as shown in Figure 5.2-1 for group A and Figure 5.2-2 for group B. The spectra graphs show "Yield [counts]" (logarithmic vertical axis) verses "Energy [keV]" (linear horizontal axis) and graphically display the concentration of x-rays hitting the detector at a wide range of energies. A sharp peak usually represents an element whilst a peak that is skewed or rounded usually means overlapping energies from different elements with the probability of intermingled $K\alpha$, $K\beta$ and $L\alpha$ energy peaks (see Appendix II for X-Ray Emission Lines).
Figure 5.2-1 X-ray spectra from PIXE analysis for group A as a function of deposition time.
Figure 5.2-2 X-ray spectra from PIXE analysis for group B as a function of deposition time.
All the spectra in Figure 5.2-1 and Figure 5.2-2 have had background intensities calculated and displayed. The software also deconvoluted most of the combination waveforms to reveal the hidden peaks. The silicon and calcium peaks are only partially displayed as these peaks are caused by the glass substrate and are not important in this analysis.

The series of spectra graphs for group A do show increasing intensities for cadmium and sulphur as the deposition proceeds but the change in peak height is only slight. The sulphur peak is sharp and well defined whereas the cadmium peak appears to be skewed. For group B spectra, both sulphur and cadmium show a rapid increase in slides 1 and 2 and then appear fairly constant in the next four slides. In slide 1, sulphur is the dominant element of the two, though in slide 2 the cadmium intensity has increased by a larger magnitude than the sulphur intensity. Other elements that are present (but not labeled) in all the slides are silicon $\text{Si}$ and calcium $\text{Ca}$ which are elements found in the glass slides.

The majority of the slides display prominent amounts of arsenic (see the As symbol in Figure 5.2-1 and Figure 5.2-2). This arsenic was verified as being part of the glass slide and not the CdS thin film, by running a PIXE scan on a blank slide and observing the arsenic peak. A significant amount of iron $\text{Fe}$ was also apparent in many slides but this iron concentration reduced whenever arsenic was also found in the slides.

Further analysis with the cadmium and sulphur concentrations resulted in graphs of “Cd/S Atomic Ratio” (linear vertical axis) verses “Deposition Time – min” (linear horizontal axis) and graphically represent the changes in relative atomic ratios as the deposition proceeds. For group A (see Figure 5.2-3) the relative atomic ratio is stable at approximately 1:1 during the entire deposition while for group B the graphs show a definite prominence of sulphur at the initial stages of deposition (see Figure 5.2-4). The
ratio quickly increases to near unity at about the 40 minute mark, after which it approximately levels out, averaging a ratio of 1.2:1 towards the end of deposition.

Figure 5.2-3 Cd:S atomic ratio verses deposition time for two group A experiments where initial thiourea concentrations differed.

Figure 5.2-4 Cd:S atomic ratio verses deposition time for two group B experiments where initial thiourea and cadmium concentrations differed.
Additional graphical information was also produced for group A as shown in Figure 5.2-5 and for group B as shown in figure 5.2-6. These graphs were possible by making the assumption that CdS was the compound deposited on the slides and that this CdS had a density of 4.82 g/cm³ (Streetman & Banerjee, 2000, p.524). The graphs display “Calculated Thickness (nm)” (vertical axis) verses “Deposition Time (min)” (horizontal axis) and represent the approximate thickness of the CdS films as the deposition proceeds.

![Graph showing calculated changes in film thickness with time for group A where the initial thiourea concentrations differed.](image_url)

Figure 5.2-5 Graphs showing calculated changes in film thickness with time for group A where the initial thiourea concentrations differed.
Figure 5.2-6 Graphs showing calculated changes in film thickness with time for group B where the initial concentrations of cadmium and sulphur differed.

Each graph in Figure 5.2-5 appears to show two different rates of growth for the CdS films. For both graphs, the initial growth rate is high which then reduces markedly, approximately half way through the deposition process.

Again, each graph in Figure 5.2-6 also appear to show two different growth rates for the CdS films. Similarly, both initial growth rates are high when compared to the latter reduced growth rates which occur approximately half way through the deposition process.

These different rates of growth possibly represents two different phases of the deposition process, the transition from the ion-by-ion deposition phase to a particulate deposition phase. When comparing film thickness at the end of deposition, group B films are a minimum of 1.5 times the thickness of group A films.

Another curious observation was that all the slides that had undergone PIXE analysis displayed a circular darkened spot. By applying the proton ion beam onto a clean non-
deposited slide this dark spot was reproduced. This verified that the glass optical characteristics of the slide were being affected by the proton ion beam but did not indicate whether the CdS film was also being affected.

5.3 RBS analysis

With the RBS analysis a series of energy spectra for both groups were obtained showing "Counts" (vertical axis) versus "Energy" (horizontal axis) where energy represents the kinetic energy of the back-scattered particle. The series of RBS energy spectra in Figure 5.3-1 represent the CdS films at successive deposition times and shows two distinct peaks towards the high end of the energy scale.

![Figure 5.3-1 RBS energy spectra of Counts versus Energy for a group B experiment.](image)

The influence of the increasing sulphur concentration could not be discerned as its signal had merged into the silicon signal, but the effects of the increasing cadmium concentration can easily be seen as shown in Figure 5.3-2 which is an enlarged section of Figure 5.3-1.
Figure 5.3-2 Highlighted RBS graph of energy spectra of Counts verses Energy for a group B experiment.

The energy signal from the cadmium (approximate energy range of 1.4 to 1.7 MeV) increases at a high rate in the first two films (20 minutes and 30 minutes), after which this rate of increase reduces significantly for the remaining films (40 minutes to 60 minutes). Also there appears to be significant differences with the first two energy spectra when compared with the rest of the energy spectra in the energy range of 0.5 to 1.2 MeV. The simulation sub-program of the RUMP software was used to simulate a soda lime glass substrate having a percentage concentration of $O : 60\%$, $Si : 25\%$, $Na : 10\%$, $Ca : 3\%$, $Mg : 1\%$, and $Al : 1\%$ in combination with the $CdS$ material. The simulated curve is smooth and
closely follows the actual energy spectra for a CdS film deposited on a soda-lime glass slide as shown in Figure 5.3-3.

After examining all of the 28 RBS energy spectra available, it was concluded that the majority of glass slides were soda-lime glass but that there were some boro-silicate glass slides (O : 60%, Si : 26%, B : 9%, Na : 3%, and Al : 1%) that had mistakenly been used in the CBD experiments. It was also evident that the first two slides in the series shown in the previous Figure 5.3-2 were actually boro-silicate glass slides, which accounted for the
difference of spectra at the lower spectra energies. In Figure 5.3-4 is the direct comparison of two spectra from group B representing two slides from the same CdS CBD experiment.

![RBS energy spectra graph]

**Figure 5.3-4** RBS energy spectra of Counts verses Channel/Energy showing a soda-lime glass slide and a boro-silicate glass slide from the same group B experiment.

Areas of notable difference that are not attributed to the difference in cadmium concentrations occur at channel numbers 180, 260 and 300. Further examination of the RBS energy spectra graphs revealed that all of group A peaks were thinner than groups B peaks. Also, all group A spectra show well defined sharp peaks whereas the majority of group B peaks were ragged, having no definition at all.

### 5.4 XRD analysis

With the Grazing Incidence XRD analysis, a series of spectra graphs for each experiment were obtained (one spectra resulting from each slide) as shown in Figure 5.4-1 for group A and Figure 5.4-2 for group B.
Figure 5.4-1 Grazing Incidence XRD spectra series from group A.
Figure 5.4-2 Grazing Incidence XRD spectra series from group B.
These spectra plots show "Intensity (Yield)" on the vertical axis against "2θ Degrees" on the horizontal axis and graphically represent points of constructive interference from planes within the CdS film structure. The MDI Jade 5.0 software was used to apply minimal smoothing to the waveforms as well as to highlight and calculate the atomic distances (d) for all prominent peaks.

The series of spectra graphs for group A are all very similar, having a very prominent peak at 26.9° and lesser peaks at 23°, 52.5° and 44.4°. The 60 minutes deposition film does show a large background noise signal which has almost swamped the peaks at approximately 52.5° and 44.4° and is the result of the detector scan running for only 3.5 hours instead of the usual 24 hours. This particular spectra also has a peak forming at 23° but because of the background noise the software failed to identify it. Attempts were made to strip away this background noise but unfortunately it made the resulting waveform unusable. The 80 min deposition film in the series displays a nicely formed peak at 26.8° with a high signal to noise ratio and was used to recalculate the 2θ angles and d values obtained from the grazing incidence analysis. This recalculation was required due to the slight 2θ angle shift that occurs with grazing incidence XRD and the recalculated data is shown in Table 5.4-1. Because all of group A spectra were near identical only the information from one spectrum is shown.

Table 5.4-1 Reference XRD data and analysis XRD data.

<table>
<thead>
<tr>
<th>Reference</th>
<th>JCPDS-ICDD</th>
<th>Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 theta</td>
<td>d</td>
<td>l</td>
</tr>
<tr>
<td>24.81</td>
<td>3.59</td>
<td>62</td>
</tr>
<tr>
<td>26.51</td>
<td>3.36</td>
<td>91</td>
</tr>
<tr>
<td>26.50</td>
<td>3.36</td>
<td>100</td>
</tr>
<tr>
<td>43.68</td>
<td>2.07</td>
<td>110</td>
</tr>
<tr>
<td>43.90</td>
<td>2.06</td>
<td>220</td>
</tr>
</tbody>
</table>
Comparisons to the reference data resulted in two matches only, one at the $2\theta$ angle of $26.5^\circ$ and the other at $44.0^\circ$, though the second match is accepted since there is some inaccuracy in the new angle calculations.

The group B spectra look very different though they are from the same deposition experiment. All the spectra are displaying prominent peaks roughly at the same $2\theta$ positions that the group A films displayed but in addition are displaying various other peaks. Only the 50 minute deposition film in group B shows a good match for the group A films. The 30 minute and 60 minute deposition films show a large number of peaks that could be the result of the x-rays penetrating into the glass slide but which requires closer examination. Comparisons with JCPDS-ICDD XRD data obtained from Gluszak (1996) proved difficult. The large peak was assumed to be the $26.5^\circ 2\theta$ position so an adjustment of $2.5^\circ$ was made to all peaks though, even with this adjustment, only a few matches corresponded to CdS. The $2\theta$ peak positions that matched are the $26.5^\circ$ cubic/hexagonal peak, the $24.81^\circ$ hexagonal peak and the $43.39^\circ$ cubic peak. In the last three spectra (60, 70, and 80 minutes) the $\text{CdSO}_4$ peak at the $20.45^\circ$ position is also matched.

5.5 AFM analysis
The AFM measurements enabled the creation of micrographs of small sections of the CdS surface for group A as shown in Figure 5.5-1 and for group B as shown in Figure 5.5-2. A clean glass slide was also given a AFM surface scan (see Figure 5.5-3) at the same magnification as the AFM scans in Figure 5.5-1 and Figure 5.5-2 in order to act as a reference.
Figure 5.5-1 AFM surface scan of a group A CdS film at 20 minute deposition time.

Figure 5.5-2 AFM surface scan of a group B CdS film at 30 minute deposition time.
Figure 5.5-3 AFM surface scan of a clean non-deposited glass slide.

The graphical displays show the surface of each CdS film with a 3 dimensional perspective where height (z vertical axis) is measured at 200 nm per division and width (x horizontal axis) is measured at 500 nm per division. Additional information is supplied such as light angle, view angle, and scan rate.

The group A scan shown in Figure 5.5-1 displays numerous nucleation sites (grains) of CdS material that are small and fairly rounded. There are areas of this scan that compare closely to the non-deposited soda-lime glass scan shown in Figure 5.5-3. Other interesting areas of the group A scan are the obvious pin hole where deposition has not occurred and also, the small number of large particulate (white caps) that reside on the surface. A side view profile gives a better idea of the surface roughness as shown in Figure 5.5-4.
Figure 5.5-4 AFM section analysis of the 20 minute deposition group A film.

The display in Figure 5.5-4 for the group A film shows the side-view plot with associated calculation tables and a vertical look-down display of the surface where the pin hole can easily be seen. Only one section line was used to obtain information about the nucleation sites but caution must be used with the side-view display as the vertical scale is approximately 4 times larger than the horizontal scale, thus distorting the true picture which, in reality would appear much smoother and flatter as shown in Figure 5.5-5.

Figure 5.5-5 Corrected relative scale of AFM section analysis side-view for the 20 minute deposition group A film
With this adjusted view, the crystal growth formation of the CdS appears to display monolayer growth with some possible island growth and also, the surface plane in this small section does appear level.

The group B scan shown in Figure 5.5-2 displays nucleated grains of CdS material though these grains appear much larger and not as numerous as the nucleated grains found in the group A film. The nucleated grains found in group B also appear less rounded and the surface looks much rougher when compared against the group A film. There appears to be a crest of nucleated sites that runs down the middle of the micro-graph and one large particulate that is very prominent, exhibiting a white cap that indicates height above the surface. The section analysis side-view for the group B film shown in Figure 5.5-6 displays this surface contour graphically and there does appear to be a crest of grains in the centre of the graph.

![AFM section analysis of the 30 minute deposition group B film](image-url)
The side-view from Figure 5.5-6 is shown with both scales equal in Figure 5.5-7.

Figure 5.5-7 Corrected relative scale of AFM section analysis side-view for the 30 minute deposition group B film.

As the deposition process continues the nucleated grains grow in size as shown in Figure 5.5-8 and Figure 5.5-9.

Figure 5.5-8 AFM surface scan of a group B CdS film at 40 minute deposition time.
Figure 5.5-9 AFM section analysis of the 40 minute deposition group B film.

By putting the same scaling on the vertical axis and horizontal axis for the side-view from the Section Analysis in Figure 5.5-8, a more accurate picture of what the surface looks like is obtained as shown in Figure 5.5-9.

Figure 5.5-10 Corrected relative scale of AFM section analysis side-view for the 40 minute deposition group B film.

This surface shows a much greater variation in depth and appears to indicate that the CdS film formation process is not monlayer formation but possibly particulate formation.
5.6 ESCA analysis

With ESCA analysis, spectra graphs for each group were obtained that display the intensity of photoelectrons recorded, in counts per second, as a function of these photoelectrons binding energy emitted from the surface of the thin films. Two films were analysed from group A and represent the state of the CdS deposition process at the 20 minute point and the 60 minute point of the same CdS deposition process. Two films were also analysed from group B and represent the state of the CdS deposition process at the 30 minute point and the 40 minute point of the same CdS deposition process. The initial spectra graphs were produced by scanning over a energy range of 0 eV to 1400 eV and enabled the identification of elements present as shown in Figure 5.6-1 for group A and Figure 5.6-2 for group B. These survey scans also enabled the calculations of relative atomic and mass concentrations for each film as shown in Table 5.6-1.

The two spectra survey scans for group A are near identical, both scans having six elements identified as appearing on the surface of the film. Of the identified elements, cadmium produces the largest peak whereas sulphur S and oxygen O show very small peaks. Zinc Zn and sodium Na are almost lost in the background. The calculated mass concentrations for group A, as shown in table 5.6-1, confirm this similarity of spectra. The identical nature of the two films, from the 20 minute deposition point to the 60 minute deposition point, indicates that conditions during the CdS deposition stayed fairly stable.

The two spectra survey scans for group B show noticeable differences in intensity for the six identified elements. The elements sodium, oxygen and silicon show a decrease of intensity with deposition time whereas the cadmium and carbon show an increase of intensity with deposition time. In both spectra, the intensity from sulphur is too small to accurately state what is happening. Table 5.6-1 also shows this change between films.
Figure 5.6-1 ESCA survey scans of two group A CdS deposited films at the 20 minute and 60 minute points respectively.
Figure 5.6-2 ESCA survey scans of two group B CdS deposited films at the 30 minute and 40 minute points respectively.
Table 5.6-1  Relative atomic and mass concentrations for group A and group B.

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<thead>
<tr>
<th>Peak</th>
<th>Position BE (eV)</th>
<th>Atomic conc %</th>
<th>Mass conc %</th>
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<td>Cd 3d</td>
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<td>O 1s</td>
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<tr>
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<th>Atomic conc %</th>
<th>Mass conc %</th>
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<td>Si 2p</td>
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<table>
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<th>Peak</th>
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<th>Atomic conc %</th>
<th>Mass conc %</th>
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</thead>
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<td>5.18</td>
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<tr>
<td>Si 2p</td>
<td>103.4</td>
<td>0.97</td>
<td>1.51</td>
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The survey scans allowed more selective scans of the elements identified (see Figure 5.6-3) so that a more precise measurement of the peak binding energies could be ascertained.
Figure 5.6-3 Close up scans of identified elements are C 1s, Cd 3d, O 1s, S 2p, and Zn 2p respectively.
The carbon atom labeled as "C 1s" on all the survey spectra was used for calibration (284.8 eV) and was found to be shifted 2.9 eV's lower than expected (due to a slight surface charging problem). This required all measured peaks to be adjusted accordingly and these adjusted peak energies were placed into Table 5.6-1 which allowed further analysis using the NIST XPS database (Wagner, et al.) for chemical compound identification.

These selective scans as shown in Figure 5.6-3 reveal that the Cd 3d peak at 405.1 eV is very sharp so a very accurate measurement can be made of its binding energy. This is also the case with the C 1s peak at 284.8 eV and is why it is often used as a standard reference point for calibration. The spectra for O 1s, S 2p, and Zn 2p are not distinct so there is difficulty in determining accurate binding energies which made it difficult to match against the NIST database. By using the NIST database and comparing the binding energies obtained from the ESCA scans against the binding energies for given compounds, a number of matches for compounds on the surface of the film were obtained as shown in Table 5.6-2.

Table 5.6-2 Binding energy of elements with NIST database matches.

<table>
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<tr>
<th>Group A - 20 minutes deposition point</th>
<th>Group A - 60 minutes deposition point</th>
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</tr>
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<td>------</td>
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<tr>
<td></td>
<td>BE (eV)</td>
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<td>Na 1s</td>
<td>1071.9</td>
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<td>Cd 3d</td>
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<td>O 1s</td>
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<td>C 1s</td>
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<tr>
<td>S 2p</td>
<td>161.9</td>
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<tr>
<td>Zn 2p</td>
<td>1022.4</td>
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</table>

121
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<th>Position</th>
<th>Match</th>
<th>Peak</th>
<th>Position</th>
<th>Match</th>
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</thead>
<tbody>
<tr>
<td>Na 1s</td>
<td>1072.4</td>
<td>( Na_2SO_4, Na_2O )</td>
<td>Na 1s</td>
<td>1071.9</td>
<td>none</td>
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<td>Cd 3d</td>
<td>405.1</td>
<td>( Cd(OH)_2, CdS, CdCO_3 )</td>
<td>Cd 3d</td>
<td>405.1</td>
<td>( Cd(OH)_2, CdS, CdCO_3 )</td>
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<td>SiO₂</td>
<td>O 1s</td>
<td>531.9</td>
<td>CdCO₃</td>
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<tr>
<td>C 1s</td>
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<td>C 1s</td>
<td>284.8</td>
<td>C</td>
</tr>
<tr>
<td>S 2p</td>
<td>161.9</td>
<td>( CdS, Na_2S )</td>
<td>S 2p</td>
<td>161.9</td>
<td>( CdS, Na_2S )</td>
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<tr>
<td>Si 2p</td>
<td>103.4</td>
<td>SiO₂, SiS₂, ( SiO₂/Si )</td>
<td>Si 2p</td>
<td>103.4</td>
<td>SiO₂, SiS₂, ( SiO₂/Si )</td>
</tr>
</tbody>
</table>

5.7 CBD Experiment analysis

The experimental setup that was used for both groups (see Figure 5.8) had some problems that hindered the CBD experimental procedure.

Figure 5.8-1 Picture of the CBD setup used by both groups.
• Access to the top of the deposition bowl was very restrictive so it was not easy to extract the slides as the experiment progressed. The stirrer had to be turned off each time a slide was to be extracted due to the high probability of the stirrer’s propeller striking and breaking the slide. Pouring the solutions of cadmium and thiourea into the deposition bowl proved difficult.

• The stirrer motor unit operated on 240 volt s ac and was controlled by a household fan controller that only had 5 settings. This made it difficult to control the fans speed, so that there was vigorous stirring without the creation of aeration bubbles.

• Controlling the temperature of the deposition bowl proved to be difficult even though the heater was a low wattage unit. Group B could only achieve a temperature control of 60±4°C whilst group A managed a temperature control of 60±0.5°C.

• The deposition bowl tended to unseat itself from the base of the water bath due to the vibrations from the stirring action.

• The original deposition bowl was made of Pyrex with placements for 4 slides. These placements were not flat or well fashioned, which made it difficult to peg the glass slides in the deposition bowl securely so that there was no side movement.

• The experimental setup made it very difficult to modify the CBD experiment. Some modifications that could prove very interesting with CBD, are microwave heating during deposition, deposition in high uniform electric fields, deposition in high uniform magnetic fields, deposition during forced resonant vibrations of the glass substrate and combinations of the latter three ideas.
Chapter 6  Discussion

6.1  \textit{CdS} Growth Phases via the CBD method

The RBS analysis revealed that bulk \textit{CdS} was in the film by comparing recorded spectra with the simulation waveform generated by the RUMP software. Unfortunately, only the cadmium produced peaks that were distinct while the sulphur remained hidden by the silicon waveform. The RBS analysis also showed that somehow boro-silicate glass slides and sod-lime glass slides were used in the same experiments. Though only cadmium peaks could be resolved the effect of the increasing cadmium could easily be seen. The peaks generated by group A films were consistently thinner than group B films, indicating that the nucleated grain sizes of group A were also smaller.

PIXE analysis revealed the changing cadmium and sulphur concentrations with respect to deposition time and enabled calculations of \textit{CdS} film thickness as a function of deposition time. The displayed graphs of “Calculated Thickness verses Deposition Time” created for group A (see PIXE analysis section, Figure 5.2-5) are acceptable on the assumption that approximately all the cadmium is combined with the sulphur to form \textit{CdS}. This assumption can be used simply because of the near unity of the cadmium to sulphur atomic ratio during the entire deposition process. This assumption does not hold for group B’s thin films, as the PIXE analysis, AFM microscope display and AFM topological diagrams show an initial sulphur deposit that is devoid of cadmium. Therefore allowances must be made in the calculated thickness of the \textit{CdS} thin film and it should be also noted, that this \textit{CdS} film is lying on top of a very thin sulphur film. With both group A and group B there was a distinct change in the rate of \textit{CdS} deposition and possibly represents two different phases of the deposition process, the transition from the ion-by-ion deposition to the particulate deposition. The PIXE analysis caused a change in the optical properties of
the glass so it is also possible that the proton ion beam caused changes to the CdS film. When using other analysis techniques this dark spot was usually avoided.

The AFM analysis directly displayed the growth of the CdS material as a function of deposition time. Micrographs of small, fairly flat and relatively round nucleated grains to much larger, rougher particulate type structures were obtained, as well as surface orientation, surface roughness, and pin hole structures. Also for this group, whilst observing the scanning process via the screen display microscope, it was observed that the scanning tip could easily break away small sections of the film indicating very weak chemical bonds. Using the screen display microscope it was simple to see the initial sulphur layer on the glass surface with a CdS layer on top.

ESCA analysis has shown that many compounds can be found on the surface of CdS thin films produced by CBD. This is hardly surprising, considering the number of different chemicals that are used in the process and the relative lack of control of the reaction processes once the chemicals are combined. A large presence of carbon was observed on the films but this was verified as contamination by sputtering off the top layers of the films and scanning again. The contamination comes from most sources i.e. simply touching or breathing produces high carbon contamination. The ESCA analysis also showed that there are definite differences in the deposition process between group A and group B. Whereas group A film surfaces changes are relatively static, group B surfaces are quick to change.

XRD analysis proved to be difficult in the running of the actual experiments and in the quality of the spectra obtained. For group A the waveforms are virtually the same spectra and both types of crystal structures (cubic and hexagonal) are identified. For group B spectra, there is a big variation in the peaks displayed and the position of these peaks. Hexagonal and cubic peaks for CdS are identified but there are obviously other compounds producing extra peaks and further investigation of these spectra is required. There were
many physical problems with this particular analysis and it is possible that the data for some of the films is suspect. After adjustment of the peak positions, cubic and hexagonal peaks for CdS can be identified as well as a peak for CdSO₄.

6.2 CBD Experiment modifications

With the desire to physically reduce the bulkiness of the CBD experimental setup and to eliminate all of the perceived problem areas, a new design was created and tested. The resulting design eliminates most of the previous problem areas.

This new designed CBD experimental setup is a totally closed system, with a very low wattage internal heating coil, polystyrene insulation cloth, polystyrene access plugs and a polystyrene enclosure as shown in Figure 6.2-1.

Figure 6.2-1 Modified CBD setup with polystyrene lid open.
Silicon rubber is applied to areas where there is a possibility of the polystyrene coming into contact with fluids. The unit is designed to handle six glass slides and each slide can easily be removed at any time during the deposition process without having to turn off the magnetic stirrer or totally open up the unit. The magnetic stirrer is positioned on a pivot so that it does not strike the glass slides as shown in Figure 6.2-2.

![Figure 6.2-2 Schematic of modified CBD setup.](image)

The unit takes approximately 10 minutes to heat up to 60 °C and can operate at temperatures as high as 90 °C. The polystyrene insulation is effective, the unit taking approximately 9.8 minutes for a volume of 300 cm³ to reduce by 1 °C. The heating element is connected to a BTC – 2220 Fuzzy Logic PID microprocessor temperature controller which keeps the temperature of the deposition bowl to 60±0.1 °C during the entire deposition. The CBD experimental unit is now of a size where placing it in a uniform magnetic field or a uniform electric field is easily achievable. This setup also enables the specific heats of reaction to be measured for the CBD method when creating the CdS thin films.
Chapter 7  Conclusions

- The CdS thin films were found to exhibit a mixture of both cubic and hexagonal structures. Other compounds were found in minute traces on the CdS film surface though no conclusion can be made as to whether these compounds formed during or after the deposition process.
- The initial ion by ion deposition rate of cadmium and sulphur on the surface of the substrate initially appears to be much higher at the beginning of the deposition process.
- A significant change in deposition rate is observed at approximately the 30 to 40 minute point in the deposition process. This transition is thought to be a change in the type of film growth process.
- The CdS thin films created by group A (1996) are type A films. These films are high quality, showing consistent Cd to S ratios, are hard and adherent to the substrate, specularly reflecting, appear homogeneous with good coverage and have small, numerous spherical grains.
- The CdS thin films created by group B (2000) are type B films. These films are low quality, exhibiting excessive initial sulphur deposits on the substrate with a thicker CdS layer on top which resulted in the films being soft, powdery, non-adherent to the substrate, with larger non-uniform grain shapes.
- The experimental CBD setup has been significantly modified, resulting in very high temperature control, no solution loss to the outside, very little gas escape, much easier experimental runs, greater ease of CBD experiment setup and modifications, reduction in required external equipment and a reduction in the physical size of the experimental CBD setup.

End
References


Materials Data Inc. *MDI JADE 5.0* [Computer software] Livermore, California.


Appendix I  CBD Apparatus and Consumables

CBD equipment
* BTC - 2220 Fuzzy Logic PID microprocessor controller with platinum (Pr) thermocouple temperature sensor
* 240 volt, 0.25 A electric motor - Universal Electric Co.
* 240 volt motor speed control (5 settings) - Casablanca.
* Electrothermal electric heater (300 Watt)
* Adjustable height platform
* Cooling bowl - Pyrex
* Deposition bowl - Pyrex
* Clips (6) and Spacers (6)

CBD Consumables
* Boro-silicate glass slides (6 used per experiment)
* Ammonia hydroxide $NH_4OH$ 35.05 MW
* Cadmium acetate dihydrate $Cd(CH_3COO)_2(H_2O)_2$ 266.52 MW - Aldrich Chemical Company Inc.
* Thiourea $CS(NH_2)_2$ 76.132 MW - Ramprie Laboratories.
* Concentrated sulphuric acid $H_2SO_4$ 98.086 MW - Analar
* Milli-Q water

Additional Equipment
* IEC Pty Ltd. electric heater and magnetic stirrer (960 Watt)
* Ultrasonic cleaning equipment - Clean Sonic, model # HS-700T
* Evaporation flasks (1 litre) and Rinsing flasks (2)
* Electronic weight scales

Safety Equipment
* Fumehood
* Spill trays
* Rubber gloves
* Laboratory coat
* Eye glasses
* Breathing mask
### Appendix II  X-Ray Emission Lines

#### Table I  
*K*-level and *L*-level emission lines in KeV

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Bearden, (1967).
Appendix III Acronyms and Symbols

AES – Auger Electron Spectrometry.
AFM – Atomic Force Microscopy.
c – Speed of light in a vacuum $3\times10^8$ (approx. m/s)
CB – Conduction Band.
CBD – Chemical Bath Deposition.
CdS – Cadmium Sulphide.
ESCA – Electron Spectroscopy for Chemical Analysis.
eV – electron volt ($1.69\times10^{-19}$ joules).
Joule – unit of energy.
n-type – semiconductor doped with donor type atoms.
p-type – semiconductor doped with acceptor type atoms.
PIXE – Particle Induced X-ray Emission.
q$\phi$ – work function (joules).
RBS – Rutherford Backscattering Spectrometry.
SE – Spectroscopic Ellipsometry.
SEM – Scanning Electron Microscope.
SIMS – Secondary Ion Mass Spectrometry.
UV/VIS – Ultraviolet/Visible Light Spectroscopy.
VB – Valence Band.
XRD – X-ray Diffraction.