EPITAXIAL GROWTH
AND CHARACTERISATION
OF CuGaS$_2$
EPITAXIAL GROWTH AND CHARACTERISATION OF CuGaS$_2$

by

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SUMMARY

In this work, the growth and characterisation of the chalcopyrite semiconductor CuGaS$_2$ is presented. The purpose of this study is to gain a better understanding of the defect chemistry of this class of materials through a systematic study relating the structural and optical properties to the composition of thin films grown by metalorganic vapour phase epitaxy. Details associated with the optimisation of the growth process are presented in a format relating the changes in the composition and morphology to variations in the growth process. The structural properties of thin films grown on GaAs(001) substrates are described. A dominance of polycrystalline growth is found to occur for Cu-rich material, whereas near-stoichiometric to Ga-rich material is typified by epitaxial growth. Secondary phases are identified by X-ray diffractometry and Raman spectroscopy for severely non-stoichiometric material. In some cases, the formation of the cubic zincblende and CuPt polytype of CuGaS$_2$ are identified by transmission electron microscopy. It will be shown that changes in the Cu/Ga ratio of the solid strongly influence the photoluminescence response of the layers. Weak excitonic luminescence is observed for both slightly Ga-rich and Cu-rich material. Near stoichiometric layers exhibit luminescence centered at ~2.4 eV. Cu-rich layers are dominated by a line occurring at ~2.1 eV, whereas a different line at ~2.25 eV dominates for Ga-rich layers. A clear picture emerges of the radiative mechanisms dominating for Cu-rich and Ga-rich layers.
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References
CHAPTER 1
INTRODUCTION

The $A^I B^{III} C^{VI}_2$ ($A = Cu, Ag; B = Al, Ga, In; C = S, Se$) ternary chalcopyrite semiconductors have been studied since the late 1950’s. However, it wasn’t until the work of Shay and Wernick in the 1960’s, that this class of semiconductor attracted considerable attention (Shay and Wernick, 1975). Almost 50 years later, these fascinating (and complex) compounds are still studied by researchers worldwide.

In the photovoltaic industry, emphasis is directed toward the high performance of inexpensive solar cells that can serve as a long-term, viable alternative to single-crystalline silicon technology. The leading contenders in this field are the $A^I B^{III} C^{VI}_2$ chalcopyrites. The uppermost valence bands of the chalcopyrites are lifted due to the tetragonal distortion of the crystal lattice and there is a hybridisation between the noble metal $p$-electrons and the anion $d$-electrons. This provides the chalcopyrites with a band gap energy of up to 1 eV lower than their respective II-VI analogues (Shay and Wernick, 1975). This property, coupled with the tendency for these materials to have a very large absorption coefficient in relation to their respective II-VI analogue, make the chalcopyrites attractive alternatives to Si technology. The Cu-chalcopyrites of the general composition $Cu(In_{1-x}Ga_x)(S_{y}Se_{1-y})_2$, offer a wide range of band gaps from ~1.0 eV for $CuInSe_2$ to ~2.5 eV for $CuGaS_2$. Efficiencies of up to 19% have been attained using $Cu(In,Ga)Se_2$ solar cells (Contreras et al., 1999). Fig. 1.1 compares the band gap energies of some of the better-known chalcopyrites and other well known semiconductors as a function of their lattice parameters.

Several chalcopyrites can be doped both p- and n-type via intrinsic defects, but $CuGaS_2$ (the material which forms the focus of this study) can be made p-type only. Since the compound has a band gap in the green part of the spectrum, interest has been generated in the area of heterojunctions between $CuGaS_2$ and large bandgap II-VI compounds for use in optoelectronics (e.g. Klenk, 2001). These applications, however, impose certain restrictions on the degree of structural perfection required of the solid. The density of
stacking faults and point defects must be minimised through refined growth techniques and the correct crystal structure of the solid must be obtained. It has indeed been found that the $\text{A}^{I}\text{B}^{III}\text{C}^{VI}_2$ materials are able to crystallise in a variety of structures which differ only in the arrangement of the group I and group III atoms on the metal sublattice (Su et al., 1998).

![Figure 1.1](image.png)

**Figure 1.1.** Band gap energies and lattice constants of a few well-known semiconductor compounds at 300 K.

A number of different techniques have been employed to grow bulk CuGaS$_2$. A few of the more popular techniques include: growth from a stoichiometric melt (Kasper, 1972); the horizontal Bridgeman method (Choi and Yu, 1996); and the iodine transport method (Tanaka et al., 1999). Studies concerning the epitaxial growth of CuGaS$_2$, by methods such as molecular beam epitaxy (MBE) (Metzner et al., 2000); metalorganic vapour phase epitaxy (MOVPE) (Hara et al., 1987; Branch et al., 2005); and chemical vapour phase deposition (CVD) (Matsumoto et al., 1987), are not as well documented as those
for bulk crystal growth. One of the main problems regarding the MOVPE growth of the Cu-chalcopyrites, is the lack of an efficient Cu metalorganic precursor, with a sufficiently high vapour pressure. This project details the MOVPE growth of CuGaS$_2$ using the new Cu precursor, namely Cu(hfac)$_2$-Et$_3$N and the Ga and S precursors TEGa (and TMGa), and DtBS, respectively.

Despite significant progress in recent years, the current understanding of the intrinsic defects present in the material is very poor. The purpose of this work is to gain a better understanding of the defect chemistry of this class of materials through a systematic study relating the structural and optical properties to the composition of thin films grown by MOVPE.

An overview of the fundamental properties of CuGaS$_2$ will be given in chapter 2. These will include: the fundamental properties of the chalcopyrites; general band theory; phase diagrams typical to the Cu-Ga-S system; and the different structure types possible for the CuGaS$_2$ system. The expected defect chemistry as determined by photoluminescence spectroscopy will also be presented. Chapter 3 reviews the MOVPE growth process and the basic thermodynamics relevant to the system. A detailed account of the important aspects relating to the metalorganic precursors used in this study, will be given. Chapter 4 deals with the experimental techniques employed during this study. An outline of the reactor is provided and all relevant details pertaining to the system layout are given. This is followed by a short discussion regarding substrate preparation and the conditions under which the metalorganic precursors were used. Typical growth parameters are provided. Some detail is given on the characterisation techniques used in this study, which include X-ray diffractometry (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), photoluminescence (PL) and Raman spectroscopy, and Rutherford backscattering spectroscopy (RBS).

The results obtained in this study are discussed in chapters 5-7. In chapter 5 an investigation into the compositional non-uniformity across the layer surface will be presented. The effect of different growth parameters on composition and morphology is
also detailed. A comparison will be made between the RBS and EDS techniques for the effective measurement of the composition of grown films. Chapter 6 details the structural properties of CuGaS$_2$ through the use of both XRD and TEM as a characterisation technique. Changes to the structural nature of the grown layers as a result of the compositional non-uniformities discussed in chapter 5 will be highlighted. This is then followed by the influence of changing growth parameters, such as growth temperature and precursor concentration, on the epilayer quality. Possible secondary phases are highlighted and identified through the use of XRD and Raman spectroscopy. Conventional TEM and high resolution TEM results will also be presented.

The photoluminescence response measured for layers grown in this study is detailed in chapter 7. Factors affecting the types of transitions observed are discussed in some length. These factors include changes made in the I/III and VI/(I+III) ratios in the vapour phase, the growth temperature and precursor concentration. Each of the typical lines observed in both Cu-rich and Ga-rich material are studied as a function of variable laser power and variable temperature measurements. In conclusion, the nature of the dominant defects in the samples is speculated upon.
CHAPTER 2

FUNDAMENTAL PROPERTIES OF CuGaS₂

CuGaS₂ is a member of a group of $A^I B^{III} C^{VI}_2$ semiconductors called ternary chalcopyrites. Other well-known materials of this class are CuInS₂, CuGaSe₂, CuInSe₂ and CuAlS₂. Together, these semiconductors display an enormous variety of properties, which makes them promising materials for a number of applications ranging from photovoltaic cells to optoelectronic devices operating in the blue and ultraviolet part of the spectrum.

2.1 Chalcopyrite crystal structure

There are two major groups of $A B C_2$ semiconductors, namely the ternary chalcopyrites comprising the $A^I B^{III} C^{VI}_2$ compounds, where $A =$ Cu, Ag; $B =$ Al, Ga, In, Tl; and $C =$ S, Se, Te, and the ternary pnictides comprising the $A^{II} B^{IV} C^{V}_2$ compounds, where $A =$ Zn, Cd; $B =$ Si, Ge, Sn; and $C =$ P, As, Sb. Since CuGaS₂ is a member of the former class of $A B C_2$ materials, this study concentrates predominantly on the properties of these semiconductors.

CuGaS₂ can be considered an isoelectronic analogue of the better-known II-VI binary semiconductor, ZnS. Its atomic configuration is a superlattice of the well-known zincblende structure, but with three significant structural differences. Fig. 2.1 gives a clearer indication of these differences. The chalcopyrite structure (space group I$4\bar{2}$D) has two cation sublattices instead of one, which leads to two nearest-neighbour chemical bonds, A-C and B-C (Jaffe and Zunger, 1983). It is significant to note that the bond length $R_{AC}$ is not necessarily the same as the bond length $R_{BC}$. Secondly, there is a small degree of tetragonal distortion in the lattice resulting from the varying bond lengths.
Thirdly, the anions are displaced from the ideal tetrahedral site by an amount $u$ (the directions indicated by the arrows in Fig. 2.1(a)). The two nearest-neighbor bond distances are given by:

$$R_{AC} = a[u^2 + (1 + \eta^2)/16]^{1/2}$$  \hspace{1cm} (2.1)$$

$$R_{BC} = a[(u - \frac{1}{2})^2 + (1 + \eta^2)/16]^{1/2}$$  \hspace{1cm} (2.2)$$

where $a$ is the lattice constant of the zincblende unit cell. The bond length mismatch is therefore:

$$\alpha = R_{BC}^2 - R_{AC}^2$$
$$= (u - \frac{1}{4})a^2$$  \hspace{1cm} (2.3)$$
For a zincblende lattice without tetragonal distortion, \( u = \frac{1}{4} \) and the bond length mismatch disappears. The tetragonal distortion is characterised by the quantity \( \eta = c/a \). The unit vectors of the primitive cell are \((a, 0, 0), (0, a, 0), (a/2, a/2, \eta a/2)\). The cations are located at 4a and 4b, whilst the anions are located at the Wyckoff positions: 8d.

### 2.2 Band theory

The band structure of a crystalline solid is a relationship between electron energy, \( E \) and momentum, \( k \). In reality, the valence and conduction bands consist of a number of sub-bands, which are doubled when electron spin is taken into account. However, in \( A^I B^{III} C^{VI} \) compounds, the uppermost valence bands are made all the more complex due to hybridisation of the noble metal \( d \)-levels and the anion \( p \)-levels. One of the most interesting aspects of this class of materials is the participation of these \( d \)-orbital electrons of the group I transition metal in the bonding of the crystal. Cu has a ground state electron configuration of \([\text{Ar}]3d^{10}4s^1\). Just how many of these \( d \)-orbital electrons participate in the bonding of the crystal has been the subject of a number of studies.

![Figure 2.2](image.png)

**Figure 2.2.** Expected behaviour of \( d \)-levels in a tetrahedral field (Shay and Wernick, 1975).

Neumann (1983) included all of the \( d \)-electrons for his calculations, whilst Merino *et al.* (2000) derived the number of participating \( d \) electrons from values obtained from the...
band structure calculations of Jaffe and Zunger (1983; 1984). Xue et al. (2000) chose the number of $d$ electrons from values suggested by experimental data of the ordinary refractive indices, $n_o$. Whichever method is used, the band structures of the Cu-containing chalcopyrites are significantly more complex than their II-VI analogues due to the participation of these $d$ electrons. The behaviour of these $d$-levels in a tetrahedral field is schematically illustrated in Fig. 2.2.

![Generic band diagram for a group-I ABC$_2$ chalcopyrite. The shaded areas denote the major sub-bands, and numbers indicate the three internal gaps. (b) Electronic band structure of CuGaS$_2$. The major bands are labeled and the principle bandgap is denoted by the shaded area (Jaffe and Zunger, 1983).](image)

**Figure 2.3.** (a) Generic band diagram for a group-I ABC$_2$ chalcopyrite. The shaded areas denote the major sub-bands, and numbers indicate the three internal gaps. (b) Electronic band structure of CuGaS$_2$. The major bands are labeled and the principle bandgap is denoted by the shaded area (Jaffe and Zunger, 1983).

The fivefold degenerate $d$-levels split into a threefold degenerate $\Gamma_{15}$ and a twofold degenerate $\Gamma_{12}$ in a tetrahedral field, with the $p$-levels transforming as a threefold degenerate $\Gamma_{15}$. If we allow for spin then the $p$-like $\Gamma_{15}$ splits into a doublet $\Gamma_8$ above a singlet $\Gamma_7$, and the $d$-like $\Gamma_{15}$ splits into a singlet $\Gamma_7$ above a doublet $\Gamma_8$. The $d$-like $\Gamma_{12}$
also transforms as a doublet $\Gamma_9$. There will be an interaction between the two $\Gamma_{15}$ levels, causing the uppermost $\Gamma_{15}$ to be raised to a higher energy, i.e. the bandgap will be reduced. In the $A^I B^{III}C_2^{VI}$ compounds there is a distinct lowering of the bandgap energy with increasing $d$-like character (Shay and Wernick, 1975). This interaction depends inversely on the energy separation between the Cu $d$-orbitals and the anion $p$-orbitals and as a result it is expected to be stronger for the sulphides than the selenides (Jaffe and Zunger, 1983). Fig. 2.3 (a) illustrates the important aspects of the band structure of a typical $A^I B^{III}C_2^{VI}$ compound. The band structure of CuGaS$_2$ is illustrated in Fig 2.3 (b). The upper valence band has its maximum at the $\Gamma_4$ point in the zone centre and the lower conduction band has its minimum at the $\Gamma_1$ point, hence giving the material a direct bandgap. This is characteristic of all Cu-B$^{III}C_2^{VI}$ materials.

2.3 Phase diagrams

The composition of a $A^I B^{III}C_2^{VI}$ compound lies on the $A_2C-B_2C_3$ pseudobinary section. It can be represented by a point in a concentration triangle and characterised by two independent parameters, non-molecularity $\Delta m$ and non-stoichiometry $\Delta S$. The non-molecularity $\Delta m$ and non-stoichiometry $\Delta S$ are defined below (Groenink and Janse, 1978):

$$\Delta m = \left[\frac{Cu}{Ga}\right] - 1,$$

$$\Delta S = \frac{2[S]}{[Cu]+3[Ga]} - 1,$$

Fig. 2.4 schematically illustrates the ternary phase diagram for the Cu-Ga-S system. The line connecting Cu$_2$S and Ga$_2$S$_3$ represents the pseudobinary phase transition at constant temperature. This transition can be expanded as a function of temperature (illustrated in Fig. 2.5). Movement along the line between Cu$_2$S and Ga$_2$S$_3$ is accompanied by a change in the cation ratio, but does not violate the condition of 4 electrons per atom. The line SN
links regions of equal cation ratio. Hence, a movement from the stoichiometric composition CuGaS$_2$ to a non-stoichiometric composition P would consist of two parts:

1) movement from CuGaS$_2$ to Q where the cation ratio is similar to that of P (a movement along this line is characterised by the appearance of atomic defects only and a change in molecularity);

2) movement along the straight line SN from Q to P (accompanied by a change in the dominant type of charge carrier).

A change in $\Delta m$ is expected to lead to a formation of equal amounts of donors and acceptors and results in a compensated crystal. $\Delta S>0$ represents an excess of anions and leads to p-type conductivity, whilst the opposite is true for $\Delta S<0$.

The liquidus temperatures and phases present in samples prepared along the Cu$_2$S-Ga$_2$S$_3$ line are indicated in Fig. 2.5. The maximum melting temperature of the chalcopyrite phase (region I) is 1240°C, where it melts congruently. No high temperature phase transition exists. Region II represents the composition CuGa$_5$S$_8$ (known as an ordered
defect compound or ODC) with a zincblende structure. It has a wide existence range (~70-90 mol% Ga₂S₃), but is unstable at higher temperatures as indicated by a possible peritectoid decomposition near 1100°C (Kokta et al., 1976). Little more is known about this relationship, and region III and IV are not labeled but likely represent an ODC with a significantly larger unit cell than CuGa₅S₈. The ODC are derivatives of the $A^I B^{III} C^{VI}$ compounds in which an array of vacancies have been introduced. These vacancies might occupy particular crystallographic sites in the structure hence giving rise to the ordered nature of these defects.

Figure 2.5. Cu₂S-Ga₂S₃ pseudobinary phase diagram (Kokta et al., 1976). Solid curves are drawn to conform to the Gibbs phase rule and dashed curves are estimates of the solidus and solvus lines.
CuGaS$_2$ has a complicated ternary phase relationship, with a number of secondary phases possible. Fig. 2.6 illustrates this relationship as investigated at room temperature using Guinier X-ray diffraction. All shaded regions in Fig. 2.6 include the chalcopyrite phase, but a detailed analysis of the specimens near the single-phase boundary is required as the second phase lines are weak. It will be shown within the results section of this study how the weak nature of the second phase lines can cause considerable difficulties in the interpretation of the grown thin films. Compositional analysis by energy dispersive X-ray spectroscopy (EDS) can clearly suggest, for e.g., a Cu-S phase present on the thin film surface, but X-ray diffraction (XRD) lines from this phase are very weak and make interpretation difficult. The single-phase region begins at 50% Ga$_2$S$_3$ and extends to 55%
Ga$_2$S$_3$, indicating a high affinity of the chalcopyrite for excess gallium (Kokta et al., 1976). Excess S exists in the vapour phase at elevated temperatures, but can cool to an amorphous state so as not to be detectable by XRD. The covellite (CuS) and chalcopyrite phases exist for S-rich conditions and Cu-rich conditions, with a Cu mole fraction of between 0.20 and 0.30, and a S mole fraction of between 0.50 and 0.55. A mole fraction of Cu greater than 0.3 and S-poor conditions promote the formation of the chalcocite phase in addition to the covellite and chalcopyrite phases. Ga- and S-rich conditions promote the formation of the CuGa$_5$S$_8$ zincblende structure. The phase diagrams in Figs. 2.5 and 2.6 were constructed from a detailed analysis of bulk samples prepared by the melt-growth technique at a temperature in excess of 1245 °C (Kokta et al., 1976). No similar study has been done to clarify the phase transitions for epitaxial CuGaS$_2$.

A study of the binary phase diagrams of the Cu-S, Ga-S and Cu-Ga systems leads to a better understanding of the possible secondary phases, which can form at a particular temperature. For the sake of brevity these phase diagrams have not been included but can be found in any comprehensive materials handbook (Davis, 1990). A shortened list of possible phases (metastable and stable) will be detailed later in chapter 6, but there are, quite simply, too many phases for these three elements alone to include a complete list. However, many of these are analogous to one another and/or are only formed under conditions not pertinent to this study (high pressure, etc.).

2.4 **Conductivity type and defects**

It is well established that the conductivity of CuGaS$_2$ is only p-type (Yu et al., 1974), which is connected to the predominance of one type of defect, apparently Cu vacancies (Horig et al., 1979; Yu et al., 1974). In most A$^1$B$^{III}$C$_2$VI compounds the conductivity can be both n- and p-type and may change depending on annealing conditions, deviations from stoichiometry and molecularity or doping. The likelihood of p-type conductivity increases upon substitution of the group VI element with S→Se→Te (see Table. 2.1). On substituting of the group I elements, Cu→Ag and the group III elements Al→Ga→In, the likelihood of p-type conductivity decreases.
Table 2.1: Conductivity types in the I-III-VI$_2$ compounds (Rogacheva et al., 1998).

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<td>CuAlS$_2$</td>
<td>p</td>
<td>CuGaS$_2$</td>
<td>p</td>
<td>CuInS$_2$</td>
<td>p-n</td>
</tr>
<tr>
<td>CuAlSe$_2$</td>
<td>p</td>
<td>CuGaSe$_2$</td>
<td>p</td>
<td>CuInSe$_2$</td>
<td>p-n</td>
</tr>
<tr>
<td>CuAlTe$_2$</td>
<td>p</td>
<td>CuGaTe$_2$</td>
<td>p</td>
<td>CuInTe$_2$</td>
<td>p</td>
</tr>
<tr>
<td>AgAlS$_2$</td>
<td>n</td>
<td>AgGaS$_2$</td>
<td>p-n</td>
<td>AgInS$_2$</td>
<td>n</td>
</tr>
<tr>
<td>AgAlSe$_2$</td>
<td>n</td>
<td>AgGaSe$_2$</td>
<td>p-n</td>
<td>AgInSe$_2$</td>
<td>n</td>
</tr>
<tr>
<td>AgAlTe$_2$</td>
<td>p</td>
<td>AgGaTe$_2$</td>
<td>p</td>
<td>AgInTe$_2$</td>
<td>p-n</td>
</tr>
</tbody>
</table>

Doping has been attempted by a number of groups in the recent past. Honda et al. (1998) investigated p-type doping of MOVPE-grown CuGaS$_2$ with phosphine and arsine as acceptor impurities. The carrier concentration was increased from 5x10$^{15}$ to 5x10$^{16}$ cm$^{-3}$ when doped with phosphine. The increase achieved by arsine doping was less significant, possibly due to the arsenic creating a deeper acceptor than phosphorus.

Li et al. (1992) investigated the effect of Fe$^{3+}$ incorporated into the CuGaS$_2$ lattice. It was shown by this study that the Fe ions substitute both the Cu and Ga sites in the crystal lattice, forming two types of defects, i.e. Fu$_{Cu}$ and Fe$_{Ga}$, the former being responsible for an infrared luminescence at 2µm, and the latter being responsible for the green colouration of crystals often reported for near stoichiometric CuGaS$_2$.

Doping of CuGaS$_2$, prepared by the Iodine Transport (IT) method, with Zn has been reported by Ooe et al. (1990). Several isolated levels were shown, a common shallower level at ~70 meV and three deeper levels at ~120, ~155 and ~205 meV. The defects assigned to the ~70 and ~120 meV levels were Zn$_{Cu}$ and Zn$_{Ga}$ respectively, whilst the level of either ~155 or ~205 meV is due to the nearest neighbor associations of Zn on Ga sublattices with S vacancies, and the other is due to Ga vacancies.
2.5 X-ray diffractometry

X-ray diffraction is commonly used in the structural characterisation of crystalline material. There have been many studies to make use of this method owing to its versatility and ease-of-use. Analysis by XRD is usually sufficient to obtain the necessary information regarding the structure and crystallinity of the grown material. However, this is not always the case for the $A^I B^{III} C^VI$ compounds.

The possible formation of the ODCs in addition to the formation of $Cu_xS_y$ and $Ga_xS_y$ phases for non-stoichiometric layers has already been discussed. However a number of different structure types are possible for the stoichiometric samples, which differ only in the arrangement of the cations within the unit cell. These structures are illustrated in Fig. 2.7.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Name</th>
<th>Space Group</th>
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<tbody>
<tr>
<td>Zincblende</td>
<td>$F\bar{3}m$</td>
<td></td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>$I\bar{4}2d$</td>
<td></td>
</tr>
<tr>
<td>CuAu</td>
<td>$P\bar{3}m2$</td>
<td></td>
</tr>
<tr>
<td>CuPt</td>
<td>$R\bar{3}m$</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.7. Crystal structures possible in the $A^I B^{III} C^VI$ system compared with the well-known zincblende structure. The group I and group III cations are represented as the solid (●) and hatched (◊) spheres respectively, whilst the anions are represented by the open spheres. One set of alternating cation planes are highlighted in blue.

The tetrahedral arrangement of cations around individual anions obeys the relationship: $Cu_nGa_{(4-n)}$, where $n = 1, 2, 3, 4$. Studies by Wei and Zunger (1989, 1990) have shown that a minimum energy is expended when $n = 2$ and the octet rule is obeyed. These authors
also showed that the chalcopyrite structure, which is characterised by alternating (201) planes of cations on the cubic metal sublattice, is the most thermodynamically stable structure at low temperatures. There is another type of ordering that still obeys the octet rule (i.e. \( n = 2 \)): the CuAu-type ordering (space group \( \text{P} \overline{4} n 2 \)) has alternating planes of cations in the [001] direction. The formation energy for this structure in CuInS\(_2\) differs from the chalcopyrite structure by only 2 meV/atom (Wei et al., 1999). If these metal atoms exhibited a disordered arrangement, but still obeyed the octet rule, then no tetragonal distortion would occur within the unit cell. This cubic structure is termed disordered zincblende. The CuPt-type ordering (\( \text{R} \overline{3} m \)) is another well-known structure where the cations alternate in planes equivalent to the (111) planes in the cubic structure. The octet rule is not obeyed for this structure and instead of the \( \text{A}_2\text{B}_2 \)-type tetrahedra, \( \text{A}_3\text{B} \)- and \( \text{AB}_3 \)-type tetrahedra occur. The formation energy for this type of ordering in CuInS\(_2\) is significantly higher than that for both the chalcopyrite and the CuAu-type ordering (Su & Wei, 1999). It is important to note that each of these structure types can have identical compositions whilst still maintaining their individuality.

The XRD spectra for some of these structure types are illustrated in Fig. 2.8. The top spectrum (a) illustrates the expected peak positions for a powder sample of CuGaS\(_2\). The 112 peak is most dominant for polycrystalline material, whereas material grown epitaxially on GaAs(001) substrates would exhibit either the 200 or 004 reflections (or both) depending on whether the \( a \)-axis or \( c \)-axis is aligned perpendicular to the 001 substrate surface. The splitting that occurs between the 220 and 204, and 312 and 116 peaks is as a result of the tetragonal distortion present in the chalcopyrite unit cell. The spectrum labeled (b) in Fig. 2.8 is the expected XRD spectrum for material having a disordered zincblende structure. Of particular interest is the lack of splitting in the 220 and 311 peaks owing to the cubic nature of the disordered zincblende unit cell. The spectrum for material exhibiting a CuAu-type ordering has been excluded due to its similarities with the spectrum for material with a chalcopyrite-type ordering. However, one significant difference exists with that of the chalcopyrite structure. The selection rules for the chalcopyrite unit cell are: \( h + k + l = 2n \) and if \( h = k \) then \( 2h + l = 4n \), but for CuAu-type ordering the selection rules become: \( h + k = 2n \), where \( l \) is arbitrary (Hahn et
Therefore, the normally disallowed 001, 003, 005, etc. reflections are allowed for the CuAu-type ordering. These reflections are expected at $8.42^\circ\theta$, $25.45^\circ\theta$ and $43.08^\circ\theta$ respectively. Spectrum (c) is slightly different owing to the rombohedral nature of this unit cell (trigonal indices are indicated). The similarities between the XRD spectra for each of the structures mentioned can create some confusion when attempting to interpret the XRD results. TEM diffraction patterns of epitaxial material are significantly more effective for the identification of these structures.

![XRD spectra for the chalcopyrite (a), disordered zincblende (b) and CuPt-type ordering as simulated by the CaRIne crystallography software using CuK$_{\alpha}$ radiation and lattice parameters for bulk material (Bodnar & Orlova, 1983). Trigonal indices are used in the assignment of the CuPt peaks.](attachment:2.8_XRD_spectra.png)

**Figure 2.8.** XRD spectra for the chalcopyrite (a), disordered zincblende (b) and CuPt-type ordering as simulated by the CaRIne crystallography software using CuK$_{\alpha}$ radiation and lattice parameters for bulk material (Bodnar & Orlova, 1983). Trigonal indices are used in the assignment of the CuPt peaks.

Metzner and co-workers have regularly demonstrated the epitaxial growth of chalcopyrite thin films on a variety of substrates by illustrating the splitting between the 220 and 204 XRD reflections (*e.g.* Metzner *et al.*, 2003). A study by Tiwari *et al.* (2000) of CuInSe$_2$...
epilayers grown by molecular beam epitaxy (MBE) yielded some interesting results related to the formation of the ODCs in increasingly Ga-rich samples. Although no Cu$_x$Se$_y$ phases were expected to form at that composition, it was surprising that no In$_x$Se$_y$ phases were identified either. However, a shift to higher $2\theta$ values was observed in the position of the CuIn$_x$Se$_y$ 336 reflection. Material with an approximate composition of: Cu: 13 at.%, Ga: 33 at.% and 54 at.% showed a shift in this peak from $\sim 77.48^\circ 2\theta$ for CuInSe$_2$ to $77.78^\circ 2\theta$ for CuIn$_{2.5}$Se$_4$. A further decrease in the Cu content of the solid to an approximate composition of: Cu: 11 at.%, Ga: 33 at.% and 56 at.% (CuIn$_3$Se$_5$) resulted in a further shift in this peak to $\sim 78.09^\circ 2\theta$. Increasingly Ga-rich material results in an increase in the ordered vacancy nature of the material. This leads to a decrease in the lattice parameter and an increase in the angle of diffraction for equivalent planes in the material. Material with an approximate composition of: Cu: 18 at.%, Ga: 29 at.% and 53 at.% exhibited two peaks resulting from the presence of two separate phases, namely CuInSe$_2$ and CuIn$_{2.5}$Se$_4$.

### 2.6 Optical properties

Optical spectroscopic techniques are sensitive to both the minority and majority carriers of a semiconductor. Since minority carrier properties of semiconductors such as carrier lifetime or radiative efficiency depend sensitively on material quality (i.e. defect concentration), optical spectroscopy is well suited to determine the quality of the material.

#### 2.6.1 Photoluminescence spectroscopy

This spectroscopic technique is concerned only with the radiative recombination paths of photoexcited electron-hole pairs. It is a non-destructive characterisation technique for analysing both the intrinsic and the extrinsic transitions of semiconductors. The external excitation source (typically a laser) has an energy higher than the band gap of the material in order for a high density of non-equilibrium electron-hole (e-h) pairs to be created. Fig. 2.9 schematically shows the basic transitions in a semiconductor. There are three
types of transitions, namely interband transitions, impurity/defect transitions and intraband transitions. Intrinsic transitions (a) as the name implies, are inherent to the semiconductor itself, and may involve phonons or excitons. These are named free-excitonic (FX) and bound-excitonic (BX) transitions respectively. The energies of these transitions are very close to that of the bandgap. High-energy emissions, (b) are often referred to as avalanche emissions and involve energetic or hot carriers.

Figure 2.9. Basic transitions in a semiconductor (Sze, 1985).

Transitions involving chemical impurities or physical defects are either, (c) free-to-bound (eA$^0$) and occur between the conduction band and an acceptor level, (d) bound-to-free (D$^0$h) and occur between a donor level and the valence band, (e) pair emission (D$^0$A$^0$), which occurs between a donor and acceptor level, or deep level transitions. Intraband transitions involving hot-carriers are also possible. High-energy emissions (b) and intraband emissions (g) are rare since carriers will rapidly thermalise via optical and acoustic phonon scattering. Of all these transitions, the most prominent are the FX, BX, eA$^0$, D$^0$h and D$^0$A$^0$ transitions. CuGaS$_2$ is a direct band gap semiconductor (where momentum is conserved in a simple radiative transition) and the energies (at finite temperatures) of the above transitions can be represented by the equations listed in Table 2.2. The effectiveness of this technique is further enhanced when the influence of variable excitation energy and variable temperature measurements on the optical response is investigated.
Table 2.2. Energies of dominant transitions in a direct band gap semiconductor at finite temperatures. Here, $\alpha$ is a constant with typical values of between 0.05 and 0.5, $n$ is a constant with typical values of between 1.0 and 2.0, $e^2/4\pi\varepsilon r_c$ is a Coulombic term, and $r_c$ is the spatial separation between the donors and acceptors involved (Schubert, 1993).

<table>
<thead>
<tr>
<th>Transition</th>
<th>Symbol</th>
<th>Energy</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free-excitonic</td>
<td>FX</td>
<td>$E_{FX} = E_g + 1/2 kT$</td>
<td>2.6</td>
</tr>
<tr>
<td>Bound-excitonic</td>
<td>BX</td>
<td>$E_{BX} = E_{FX} - \alpha (E_g)^n$</td>
<td>2.7</td>
</tr>
<tr>
<td>Free-to-bound</td>
<td>eA$^0$</td>
<td>$E = E_g - E_A + 1/2 kT$</td>
<td>2.8</td>
</tr>
<tr>
<td>Bound-to-free</td>
<td>D$^0$h</td>
<td>$E = E_g - E_D + 1/2 kT$</td>
<td>2.9</td>
</tr>
<tr>
<td>Donor-acceptor</td>
<td>D$^0$A$^0$</td>
<td>$E = E_g - E_A - E_D + \frac{e^2}{4\pi\varepsilon r_c}$</td>
<td>2.10</td>
</tr>
</tbody>
</table>

2.6.2 PL literature review

The optical properties of bulk crystals of CuGaS$_2$ have been investigated from as early as 1971 (Tell et al., 1971) and a thorough review of the chalcopyrite materials by Shay and Wernick was published in 1975 (Shay & Wernick, 1975). An early study of bulk crystals grown by the iodine-vapour transport (IT) method by Massé (1985), which included the annealing of the material in maximum and minimum S-overpressure and variable excitation, temperature and time-dependent PL measurements, concluded that the observed green luminescence at ~2.40 eV can be ascribed to a D$^0$A$^0$ transition. The energy levels responsible for this emission were a donor level at ~50 meV below the conduction band, and an acceptor level at ~130 meV above the acceptor band (possible a V$_{Cu}$ or a S$_i$). In this study, a broad band of red luminescence was also observed, which was ascribed to the V$_S$ associated with an additional impurity. Shirakata et al. (1990) gave a detailed account of the excitonic luminescence observed from crystals grown by both the IT- and melt-growth methods. In this paper, the line at 2.504 eV was attributed to the FX transition, whereas the lines at 2.501 eV, 2.495 eV and 2.493 eV were attributed to one donor-bound exciton (D$^0$X) and two acceptor-bound excitons (A$^0$X) exciton complexes respectively.
However, it was not until 1993 that the optical properties of epitaxial thin films were presented at the 9th International Conference on Ternary and Multinary Compounds in Yokohama, Japan (Yagi et al., 1993). The deep region emissions of films grown on GaP and GaAs substrates by vapour phase epitaxy (VPE), and bulk crystals grown by the IT-method were investigated. Emissions in the region of ~1.70 eV and 1.85 eV were ascribed to a deficiency in the group VI species during growth and the lowest energy line at ~1.40 eV was ascribed to the $V_{\text{Cu}}$ intrinsic defect. The most intense line in samples grown by VPE, that of the line at 1.85 eV, was ascribed to a $D^0A^0$ transition involving the $V_S$ and interstitial halogen atom originating from the growth process (CuCl and GaCl$_3$ precursors were used). A detailed study of MOVPE-grown CuGaS$_2$ films was reported on by Shirakata and Chichibu (2000). For epilayers grown on both GaP and GaAs substrates, excitonic-related peaks were observed in the region of ~2.49-2.50 eV. Excitation dependent studies of a peak at ~2.43 eV revealed that this line can be ascribed to a free-to-bound transition with an ionization energy of ~90 meV. A similar study of a peak at 2.40 eV revealed the $D^0A^0$-like nature of this transition. Two energies of 46 meV and 100 meV were obtained for the donor and acceptor levels involved in this transition. Suggested defects included the $V_S$ or $Ga_{\text{Cu}}$ for the donor, and the $V_{\text{Cu}}$ for the acceptor. Broad luminescence was also observed at an energy of ~1.65 eV. The effect of composition on PL was also reported by this group. It was shown that nearly stoichiometric CuGaS$_2$ exhibited the strongest exciton PL, Ga-rich epilayers were characterised by a strong $D^0A^0$-related transition at 2.40 eV, and Cu-rich epilayers exhibited a distinct broadening of band-edge luminescence.

More recent studies of the optical properties of CuGaS$_2$ epilayers grown on Si substrates by MBE include that of Eberhardt et al. (2003). This study clearly showed the dependence of the PL spectra on the composition of the grown epilayers. It was shown that for Ga-rich material, excitonic recombination is not observed, whilst a defect-related transition at ~2.4 eV is strong. Excitonic transitions and the same defect-related transition at ~2.4 eV were observed in samples that were stoichiometric and Cu-rich in nature. However, the width of the 2.4 eV line was of the order of ~30 meV (as opposed
to ~100 meV in Ga-rich samples). Broad luminescence at ~2.1 eV, assigned to deep defects, was observed for all compositions, but was reported to red-shift with an increase in the Cu/Ga ratio of the solid. In a more recent paper by this group (Metzner et al., 2004) on the same layers discussed in Eberhardt et al. (2003) it was reported that the low-temperature band gap of epitaxial material was the same as that of single-crystalline material. This was attributed to the absence of any residual lattice strain in the CuGaS$_2$/Si(111) films. Further details (including the S-termination of the Si substrate surface before growth) can be found in Metzner et al. (1996) and Metzner et al. (2001).

A total of two $D^0A^0$ and two $eA^0$ transitions are observed and ascribed to one shallow donor level ($V_S$) and two acceptor states ($V_{Cu}$ and $V_{Ga}$) at ~25 meV below the conduction band, and ~89 meV and ~109 meV above the acceptor band, respectively.

2.6.3 Raman spectroscopy

A small fraction of light (~1 in $10^7$ photons) incident on a material is inelastically scattered because of interactions with the electric dipole of a molecule. This inelastic scattering, termed Raman scattering, can change the vibrational energy of the dipole in the lattice. Most of the inelastically scattered photons have frequencies lower than the frequency of the incident light (termed Stokes scattering). However, a small portion has a frequency higher than that of the incident light, which is therefore termed anti-Stokes scattering. The difference in energy between the initial and final vibrational levels can be obtained from:

$$\nabla (cm^{-1}) = \frac{1}{\lambda_{\text{incident}}} - \frac{1}{\lambda_{\text{scattered}}}$$  \hspace{1cm} (2.11)

where the wavelengths of the incident and scattered photons are usually given in cm.

The vibrational energy is usually dissipated as heat, but owing to the low intensity of Raman scattering, this does not usually give rise to a heating of the sample during analysis. This technique is another example of a non-destructive technique that can be
used to characterise the crystallographic orientation and the chemical composition of semiconductor thin films. The changes in composition are accompanied by a shift in the phonon frequencies, whilst the orientation will affect which selection rules are obeyed for the vibrational modes imposed by the point symmetry. There are 24 modes of vibration of which only 21 modes are optical at $q = 0$ (where $q$ is the normal coordinate of the vibration) for the CuGaS$_2$ crystal (Sugai, 1977) and symmetry conditions predict that the optical modes in the crystal may be written as (Guha et al., 2003):

$$\Gamma_{\text{optical}} = \Gamma_1 + 2\Gamma_2 + 3\Gamma_3 + 3\Gamma_4 + 6\Gamma_5$$  \hspace{1cm} (2.12)

For these modes: there is one Raman-active $\Gamma_1$-mode (known as the breathing mode) which appears in all chalcopyrite structures and is always dominant (Gonzales et al., 1992; Koschel & Bettini, 1975; Carlone et al., 1980), two inactive $\Gamma_2$-modes, three Raman-active $\Gamma_3$-modes, three $\Gamma_4$-modes and six $\Gamma_5$-modes which are both Raman- and infrared-active (Kraminow et al., 1970). The $\Gamma_1$-mode is purely ionic and is caused by the vibrations of sulphur atoms whilst the rest of the atoms are stationary (Julien & Barnier, 2001). It is therefore reasonable to assume that the frequency of this mode in CuGaS$_2$ is very similar to the $\Gamma_1$ mode in CuInS$_2$ since it involves the motion of the same atom, S in this case. The frequency of this mode is given by (Rincón & Ramírez, 1992):

$$\nu = \left( \frac{k}{M_C^{VI}} \right)^{1/2}$$  \hspace{1cm} (2.13)

where $k$ is the force constant and $M_C^{VI}$ is the mass of the C$^{VI}$ atom in the A$^I$B$^{III}$C$_2^{VI}$ compound.

Of the three $\Gamma_3$ modes, the highest energy mode is generally not observed despite being Raman-active according to group theory. This is owing to the motion of the A$^I$ and B$^{III}$ atoms in antiphase with each other (Rincón & Ramírez, 1992). The frequency of this mode can be estimated by (Rincón & Ramírez, 1992):
\[ \nu = k\left( M_A^{I} + M_B^{III} \right)^{1/2} \left( M_A^{I} M_B^{III} \right)^{1/2} \]  \hspace{1cm} (2.14)

where all the symbols have their usual meaning.

The lowest-energy \( \Gamma_3 \) mode involves the \( A^{I} \) and \( B^{III} \) atoms moving in phase with each other, and the frequency of this mode can be expressed by (Rincón & Ramírez, 1992):

\[ \nu = k^{1/2} \left( M_A^{I} + M_B^{III} \right)^{1/2} \]  \hspace{1cm} (2.15)

where all the symbols have their usual meaning.

2.6.4 Raman literature review

One of the first reports on the vibrational properties of CuGaS\(_2\) as measured by Raman spectroscopy was given by Shay & Wernick (1975). Most of the studies before 1990 involved the pressure-dependence of the vibrational modes for bulk crystals of CuGaS\(_2\). The Se-containing chalcopyrites and CuInS\(_2\) have been characterised by Raman spectroscopy to a larger degree than CuGaS\(_2\), but useful observations can be made from these studies regarding the shift in peak positions as a function of composition, and the presence of additional peaks owing to secondary surface phases formed during the growth process. A list of the wave numbers of the major modes expected for CuGaS\(_2\) and their respective references are given in Table. 2.3.

To obtain an understanding of the effects of composition on the Raman spectra of CuGaS\(_2\) thin films, it is necessary to investigate the Raman spectroscopic results of other chalcopyrite materials such as CuInSe\(_2\), CuGaSe\(_2\) and CuInS\(_2\). Several authors have verified the appearance of additional bands with increasing Cu/Ga ratio in the solid (Alvarez-García et al., 2002; Guha et al., 2003; Rudigier et al., 2004). Of these additional modes, the most intense is one which appears at a frequency slightly higher
than that of the $\Gamma_1$ breathing mode. The relative intensity of this mode to that of the $\Gamma_1$ mode is directly related to the relative amounts of CuAu-ordering present amongst the chalcopyrite ordering of CuGaS$_2$.

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<td>95</td>
<td>94</td>
<td>284</td>
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<tr>
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<td>167</td>
<td>165</td>
<td>147</td>
<td>156</td>
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<tr>
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<td>276</td>
<td>283</td>
<td>-</td>
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<td>$\Gamma_1$</td>
<td>312</td>
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<td>313</td>
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<tr>
<td>$\Gamma_4^{(2)}$</td>
<td>348</td>
<td>350</td>
<td>367</td>
<td>349</td>
<td>371</td>
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<td>$\Gamma_5^{(2)}$</td>
<td>-</td>
<td>384</td>
<td>385</td>
<td>366</td>
<td>387</td>
<td>384</td>
<td>393</td>
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<td>$\Gamma_{4,5} + \Gamma_1$</td>
<td>626</td>
<td>629</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>$\Gamma_4^{(2)} + \Gamma_1$, $\Gamma_{4,5} + \Gamma_5^{(2)}$</td>
<td>660</td>
<td>664</td>
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<td>$2\Gamma_4^{(2)}$</td>
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<td>-</td>
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<td>$\Gamma_4^{(2)} + \Gamma_5^{(2)}$</td>
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<td>735</td>
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</tbody>
</table>

CHAPTER 3

THE MOVPE GROWTH PROCESS

Over the course of the last forty years, the advances made in the semiconductor industry have been enormous. Not only have an increasing variety of semiconductor materials been studied, but increasingly novel methods have been employed for their growth. Whilst liquid-phase epitaxy (LPE) and chloride vapour-phase epitaxy (ClVPE) may be the oldest of the techniques, the more advanced vapour-phase technique, namely metalorganic vapour-phase epitaxy (MOVPE) has become significantly more popular in recent years. Molecular-beam epitaxy (MBE) allows excellent control through \textit{in situ} monitoring. However, the apparatus required for the ultra-high vacuum is expensive and difficult to maintain. The purity of material grown by MOVPE and the flexibility of the process is well known within the crystal grower community; however, a number of problems are still inherent to this method. The most significant of these is the cost of the reactants required, known as metalorganics (MO), as well as their toxicity, and the large number of parameters that need to be controlled accurately in order to maintain reproducibility.

3.1 Overview of the MOVPE growth process

The MOVPE process demonstrates the use of MO precursors which are delivered to a heated reactor in the vapour phase. This is done by bubbling a purified carrier gas, usually $\text{H}_2$, through stainless steel bottles containing the appropriate MOs, where the gas will collect trace amounts of the molecules and feed them into a reactor. The MO molecules are ‘cracked’ in this region, which is typically heated, and the reactive species undergo chemical reactions with one another on/in the vicinity of the surface of the layer. The remaining organic molecule of the MO is flushed from the system. The fundamental processes that occur during crystal growth can be divided into either the thermodynamic or the kinetic components. The former establishes the driving force for the process as a whole, whilst the latter determines the rate at which the process will proceed. The growth
rate of the material system as a function of some external parameter can be categorized as either mass transport-, surface kinetics- or thermodynamically limited. For example, the orientation of the substrate has no effect on either the mass transport or the thermodynamics and as such, the dependence of the growth rate on the substrate orientation is kinetically limited.

3.2 Basic thermodynamics

In a system with constant pressure and temperature, thermodynamics defines the compositions of the different phases in the equilibrium system. Equilibrium is defined as the point at which the Gibbs free energy, $G$, is at a minimum. The Gibbs free energy is defined in terms of the enthalpy, $H$, which is related to the energy of formation for a system, and the entropy, $S$, which is related to the order of the system:

$$G = H - TS$$  \hspace{1cm} (3.1)

The enthalpy of formation is defined as:

$$H = E + PV$$  \hspace{1cm} (3.2)

where $E$ is the internal energy, $V$ is the volume, and $P$ is the pressure of the system.

MOVPE growth is essentially a non-equilibrium process. The concentration of the reactants in the gas phase is forcibly higher than the concentration which would normally exist at the substrate under equilibrium conditions at a particular pressure and temperature. This state is called supersaturation. Thermodynamically, the driving force to restore equilibrium is simply the difference in chemical potentials between the solid and vapour phases:
\[ \Delta \mu = \mu^s - \mu^v = (\mu_o^s + RT \ln a^s) - (\mu_e^v + RT \ln a^v) \] (3.3)

where the superscripts V and S denote the vapour and solid phases, respectively, \( a \) is the activity of the constituent, which is the sum of the mole fraction and activity coefficient, \( \gamma \) and the subscript \( e \) denotes the activity at equilibrium (Stringfellow, 1989).

In reality, the growth rate is significantly lower than that calculated from thermodynamics. The kinetics of the MOVPE growth process is divided into two parts, namely mass transport and the actual chemical reactions and their rates. Both of these are not fast enough to allow equilibrium to be established throughout the system at all times.

### 3.3 Mass-transport

The hydrodynamics of an MOVPE system is an extremely complex subject better understood with the aid of high-powered supercomputers and fluid-dynamics. This aspect is more dependant upon the MOVPE reactor design and pressure than any other part of the crystal growth process. Without completely revisiting this subject, one of the more important theories, the boundary-layer concept (Leys and Veenvliet, 1981) will briefly be reviewed. This concept is the most widely used model for the calculation of the growth rate in the mass-transport-limited regime. Within this concept there are three types of boundary layers, namely the velocity, thermal, and diffusion boundary layers, which will develop independently to form a single, combined boundary layer.

#### 3.3.1 Velocity profile

For a system with a flow of an isothermal, single-component fluid (e.g. \( H_2 \)), a number of boundary conditions are required in order to obtain a solution to a partial differential equation relating mass, momentum and energy conservation. The first boundary
condition stipulates that the velocity vector, \( \mathbf{v} \) is zero at the reactor wall and on the susceptor/layer surface (i.e. both the perpendicular and parallel velocity components are equal to zero). The second boundary condition defines the parallel velocity component to equal the free stream value, \( U_\infty \) at a distance infinitely far from the susceptor surface. Because of these constraints, there exists a region in which the velocity of the fluid must decrease in order to reach zero at the susceptor surface. This region is known as the boundary layer and has a thickness defined as the distance from the interface at which the velocity component parallel to the susceptor surface becomes 99% of \( U_\infty \). This concept is schematically illustrated in Fig. 3.1.

![Figure 3.1](image)

**Figure 3.1.** Development of the boundary layer over a flat susceptor in a horizontal reactor tube (Stringfellow, 1989, p. 219).

### 3.3.2 Thermal profile

There exists a difference in temperature between the heated region of the reactor (in this case the bottom) and the cooler top surface. This temperature gradient is further exaggerated if the reactor walls are water-cooled during the growth process. Fig. 3.2 schematically illustrates this concept. Upon entering the reactor (this position is considered to be \( x = 0 \)), only the layer closest to the heated surface is considered to be at the growth temperature. Thereafter, the gas temperature decreases suddenly to the ambient gas temperature typical for the top surface of the reactor.
Figure 3.2. The development of a temperature profile upon entering a top-cooled, horizontal reactor tube. A constant temperature gradient is formed at the point $x_T$. $T_G$ denotes the growth temperature (Ban, 1978).

This steep temperature gradient will decrease as the gas moves over the heated surface until a constant temperature gradient exists between the bottom and top surfaces within a certain distance (called $x = x_T$). This distance has been defined (Giling, 1985) as:

$$x_T = 0.28 h R_e$$  \hspace{1cm} (3.4)

where dimensions are in centimeters, and $R_e$ denotes the Reynolds number.

There are a number of methods for decreasing the gradient of the temperature profile and shortening $x_T$. These include heating the carrier gas before it enters the reactor, not employing water-cooling and growing under atmospheric pressure, all of which were employed in this study. Therefore, the distance $x_T$ will be considerably shorter than that predicted by Eq. 3.4 above.

3.3.3 Precursor concentration profile

It will be shown in chapter 5 that Cu is the rate-limiting species in the growth of CuGaS$_2$. The growth rate of the system would therefore be limited by the diffusion of the Cu species through the boundary layer to the growth interface. Since the concentration of the Cu species is considered constant above the boundary layer and zero at the growth
interface, a concentration profile exists perpendicular to the flow of carrier gas and reactant species. This profile is illustrated in Fig. 3.3.

![Diagram of concentration profile](image)

**Figure 3.3.** The concentration profile of individual species across the cross-sectional area of the reactor. The distance at which the gradient of the concentration profile is considered constant is denoted as $x_d$ (Ban, 1978).

At the susceptor leading edge ($x = 0$) the concentration profile is steep resulting in a high growth rate, which drops as the gradient of the profile decreases. Beyond the distance, $x_d$ the concentration gradient is considered constant across the cross-sectional area of the reactor.

### 3.3.4 Single boundary layer

Each of these boundary layers can be combined to form a single boundary (Leys and Veenvliet, 1981) schematically illustrated in Fig. 3.4. It is evident from Fig. 3.4 that an upper and lower boundary layer exists in the reactor, with the lower boundary layer increasing in thickness more rapidly than the upper. Once the two layers have joined, the flow can be considered fully laminar. The central core region can be considered a uniformly mixed reservoir of the reactant species. The concentration of reactant species decreases, however, toward the exhaust side of the reactor as species are used up. This can lead to a drop in the growth rate. A means for counteracting this problem is to elevate the trailing edge of the susceptor, thereby decreasing the cross-sectional area of the reactor. This allows for an increased average velocity and a decreased boundary layer thickness. Substrate rotation during the growth process also solves this problem.
The precursor concentration, velocity and temperature profiles can be combined to form a single boundary layer concept (Ban, 1978).

The actual growth rate measured for a system is always lower than the value obtained from thermodynamic considerations only. This has been attributed to the limiting effect of the rate of the chemical reactions occurring between the different reactant species at the growth interface. These chemical reactions will be discussed in greater detail in the following sections pertaining to the MO precursors themselves.

3.4 Metalorganic precursors

MOVPE growth has progressed to the point where the design of the source molecule is an integral part of the whole process. Basic properties such as boiling point, melting point and vapour pressure of the material can now be modified to meet the demands of the crystal grower.
3.4.1 Precursor chemistry

An important consideration for MOVPE is the energy of the metal-carbon bond in the precursor molecule, as the bond strength between these two atoms determines the stability of the molecule against decomposition by free-radical homolysis. In general, the higher the electronegativity of the metal, and the smaller the size of the radical, the stronger the metal-carbon bond strength. For example, the bond strength between the gallium and the carbon atom in trimethylgallium is of the order of 60 kcal/mole, but approximately 57 kcal/mol for triethylgallium (Stringfellow, 1989). The weakening of the carbon–metal bond in this manner is attributed to the delocalization of the free-radical electronic charge. This bond is weakened even further for the allyl radical, where a double bond is formed, and the benzyl radical, where the carbon is bonded to a benzene ring. The vapour pressure of the MO source varies significantly with the type of alkyl group. Generally, the lighter the molecule and the more branched the molecule, the higher the vapour pressure.

3.4.2 Copper precursors

In this study, two different copper precursors were used. The chemistry of these metalorganics will be discussed in slightly more detail than that of the gallium and sulphur metalorganics as it bears particular relevance to the unique results observed.

3.4.2.1 Cyclopentadienyl-copper-triethylphosphine

Cyclopentadienyl-copper-triethylphosphine, or CpCuTEP, has been the most commonly used copper MO for the MOCVD growth of all Cu-chalcopyrites in the past 20 years. It is an oxygen-free, CuI precursor, known to have an extremely low vapour pressure (VP) (Artaud-Gillet et al., 2003; supplier: Morton International) even at elevated temperatures (0.01 Torr at 60 °C). In addition to this extremely low VP, which causes problems relating to the growth rate, CpCuTEP is known to undergo a pre-reaction with a number
of different types of Group VI precursors (discussed in Section 3.4.4). Fig. 3.5 illustrates the chemical structure of this precursor.

![Chemical structure of CpCuTEP](image)

**Figure 3.5.** The structure of CpCuTEP showing the aromatic ring and the neutral P-Et₃ ligand.

The cyclopentadienyl (C₅H₆) structure on its own is non-aromatic owing to an intervening \( sp^3 \)-hybridized CH₂ group preventing delocalization of the \( \pi \) electrons. However, when this C atom loses a proton, the remaining electrons are able to \( sp^2 \)-hybridize like the rest of the C atoms in the ring leading to six delocalized \( \pi \) electrons. The Cu atom, as a result, is not strictly bonded to any particular C atom, but rather to the ring structure as a whole. The three ethyl groups bonded to the phosphine atom, P-Et₃ is a neutral organic donor ligand, which is also not bonded to the Cu atom. Previous growth studies involving the use of this precursor have usually listed the amount of Cu introduced into the reactor in terms of l/min instead of \( \mu \)mol/min as is the norm (e.g. Hara et al., 1998; Siebentritt et al., 2002; Chichibu et al., 1997; Chichibu et al., 1998; Bauknecht et al., 2000a; Shirakata and Chichibu, 2000; Harada et al., 2001; Honda et al., 1993; Artaud-Gillet et al., 2003).

### 3.4.2.2 Hexafluoracetylacetonate-copper-triethylamine

Various oxygen-containing precursors have been synthesized based upon the β-diketonate functional group. These precursors are usually written as Cu(hfac)-L, where L is a neutral, organic donor ligand such as a Lewis base (e.g. trimethylphosphine or
triethylamine), an alkene (e.g. vinyltrimethylsilane) or an alkyl (e.g. 2-butyne) weakly bonded to Cu (Fig. 3.6 (a)). They have varying properties depending on the nature of the ligand L.

**Figure 3.6.** The oxygen-containing Cu\(^+\) \(\beta\)-diketonate involves a ring-structure and a neutral ligand L (a), Cu\(^+\) \(\beta\)-diketonate (b), and Cu\(^+\) \(\beta\)-diketonate with the neutral ligand triethylamine (c).

The process by which copper is deposited is by a disproportionate reaction (see Eq. 3.5 below), where Cu\(^+\) undergoes both reduction and oxidation simultaneously. This reaction is only 50% efficient, as only half the reactant contributes toward the deposition of solid copper and occurs even at low temperatures. The other half is converted into the Cu\(^+\) \(\beta\)-diketonate, namely Cu\(^+\)(hfac)\(_2\) (Fig. 3.6 (b)). The VP of this precursor is lower than that of the Cu\(^+\) precursor, and is more stable at elevated temperatures (Choi *et al.*, 1996). Although this precursor is far less understood, it is known to undergo a reduction reaction in the presence of hydrogen (see Eq. 3.6 below) at temperatures exceeding 175 °C, but does not reach the surface-reaction-limited stage until 320 °C.

\[
2 \text{Cu}^+\text{(hfac)}-\text{L}_n \ (g) \rightarrow \text{Cu}^0 \ (s) + \text{Cu}^+\text{(hfac)}_2 \ (g) + 2n\text{L} \ (g) \quad (3.5)
\]
\[
\text{Cu}^+\text{(hfac)}_2 \ (g) + \text{H}_2 \ (g) \rightarrow \text{Cu}^0 \ (s) + 2\text{H(hfac)}_2 \ (g) \quad (3.6)
\]

The second Cu-precursor used in this study, Cu(hfac)\(_2\)Et\(_3\)N (Fig 3.2c), belongs to the latter group of Cu\(^+\) \(\beta\)-diketonates. To our knowledge, this precursor has only been investigated by one other group thus far (Artaud-Gillet *et al.*, 2003) for the MOCVD growth of CuGaSe\(_2\). The VP curve for this MO is not known, but the estimated value (Epichem Inc.) at 25 °C is of the order of ~0.25 Torr (which is significantly higher than
the value for CpCuTEP). The VP equation for Cu(hfac)$_2$ alone is given by Wolf et al., 1999:

\[
\text{Cu(hfac)$_2$: } \log_{10} P = 14.74 - \frac{5140}{T}
\] (3.7)

This equation is significant in this study since the original MO, namely Cu(hfac)$_2$-Et$_3$N was found to decompose over a period of use. In the initial stages of our experiments, the VP was found to steadily decrease over time. We were advised by the manufacturer of this source (Epichem Ltd.) that after a period of extended use the VP would cease to drop and level out at some value attributed to the modified MO, Cu(hfac)$_2$. The function of the Et$_3$N radical was thus to provide enhanced volatility to the whole molecule and increase its VP.

3.4.3 Gallium precursors

In this study the gallium precursors trimethylgallium (TMGa) and triethylgallium (TEGa) were used. The majority of the chemical reactions taking place for this MO take place homogenously in the gas phase. For the growth of GaAs, it has been shown (Field and Ghandi, 1984) that TMGa decomposes into Ga-CH$_3$ in the vapour phase in the vicinity of the heated substrate through reactions represented by Eqs. 3.8 and 3.9. Thereafter, the Ga-CH$_3$ diffuses through the boundary layer to the growth interface, where it will further decompose into elemental Ga and CH$_3$ (Eq. 3.10).

\[
Ga - (CH_3)_3 \xrightarrow{2.58\text{eV}} Ga - (CH_3)_2 + CH_3
\] (3.8)

\[
Ga - (CH_3)_2 \xrightarrow{1.54\text{eV}} Ga - (CH_3) + CH_3
\] (3.9)

\[
Ga - (CH_3) \xrightarrow{3.36\text{eV}} Ga + CH_3
\] (3.10)

One can expect the same behaviour from TMGa when used for the growth of CuGaS$_2$. The most common impurity introduced from this precursor has been shown to be carbon
in the growth of GaAs (Dapkus et al., 1981). Incorporation of this impurity into the GaAs lattice is enhanced at very low or very high growth temperatures, low V/III ratios and low pressures (Jones and O’Brien, 1997). The vapour pressure curve for this precursor is given by Stringfellow (1989).

\[
\text{TMGa: } \log_{10} P = 8.07 - \frac{1703}{T} \quad (3.11)
\]

where the pressure \( P \) is given in Torr and the temperature \( T \) is given in Kelvin.

As mentioned in Section 3.4.1, the bond strength between the gallium and carbon atom is stronger for TMGa than for TEGa, and the VP of the latter will be lower. It will be shown presently that the VP values for the copper metalorganics used in this study (and presently available on the market) are particularly low and TEGa is better suited to the growth of CuGaS\(_2\) than TMGa is. Most previous studies have involved the use of either TEGa or normal-tripropylgallium (TPGa) as a gallium precursor, not only due to their similar VP values, but due to the lower decomposition temperatures of these precursors compared to that of TMGa (Chichibu et al., 1994). The metal-carbon bond strength of the normal-tripropyl radical is similar to that of the ethyl radical and less than that of the methyl radical as can been seen from Table 3.1 (Stringfellow, 1989).

<table>
<thead>
<tr>
<th>Radical</th>
<th>Methyl</th>
<th>Ethyl</th>
<th>n-propyl</th>
<th>i-propyl</th>
<th>t-butyl</th>
<th>Allyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond strength (kcal/mol)</td>
<td>105</td>
<td>98</td>
<td>98</td>
<td>95</td>
<td>92</td>
<td>87</td>
</tr>
</tbody>
</table>

TPGa has been used successfully as a precursor, along with CpCuTEP and DtBS as the other source materials, by a group from the Science University of Tokyo (Chichibu et al., 1995; Harada et al., 2001). A group at the Tokyo Institute of Technology (Hara et al., 1987; Otoma et al., 1991; Honda et al., 1993) has used the more popular TEGa for a number of years to indeed grow CuGaS\(_2\) on a variety of substrates. The vapour pressure curve for TEGa is of the order of (Stringfellow, 1989):
The use of TEGa instead of TMGa for the growth of GaAs is said to result in parasitic reactions between TEGa and both AsH$_3$ and triethyl arsine (TEAs) (Stringfellow, 1989), however, no parasitic reactions occur between TEGa and DtBS or either of the copper precursors used in this study (Artaud-Gillet et al., 2003). The level of carbon contamination in GaAs epilayers is reduced from $10^{20}$ cm$^{-1}$ to $10^{14}$ cm$^{-1}$ (Pütz et al., 1986) when using TEGa instead of TMGa for the growth of GaAs at low temperatures as the MO molecule is completely pyrolised at higher temperatures.

3.4.4 Sulphur precursor

A number of sulphur precursors are commercially available for use in MOVPE, such as diethyl sulphide (DES), hydrogen sulphide (H$_2$S), thiophene (C$_4$H$_4$S) and methylmercaptan (CH$_3$SH). The latter three have been shown to undergo a pre-reaction with the more common copper precursor CpCuTEP, whilst the decomposition of DES was negligible at a growth temperature of less than 600 °C (Honda et al., 1993). The precursor ditertiarybutylsulphide (DtBS) was chosen for this study since it decomposes sufficiently at growth temperatures above 450 °C and does not undergo any pre-reaction with CpCuTEP, TMGa, or TEGa. It was not known prior to this study whether DtBS undergoes a pre-reaction with Cu(hfac)$_2$·Et$_3$N as the chemical properties of the latter precursor are not well known. The sulphur-carbon bond strength in DtBS is weakened compared to DES due to delocalization of the free-radical electron charge and consequently is more suited to growth at lower temperatures.

DtBS is a colourless liquid at room temperature and can be transported to the reactor by passing H$_2$ carrier gas through the stainless steel bubbler. The VP equation for this precursor is not known, but an estimated VP curve is provided by the supplier, Epichem Inc. It seems to be similar to that of the better-known ditertiarybutylselenide (DtBSe),

$$\text{TEGa: } \log_{10} P = 9.172 - \frac{2532}{T}$$

(3.12)
but the curve for DtBS is shifted by 10 °C to higher temperatures. Both curves have been plotted on a semi-log graph of VP versus bubbler temperature in Fig. 3.7.

![Figure 3.7](image.png)

Figure 3.7. Semi-log VP curves for DtBSe and DtBS as a function of bubbler temperature. A VP equation is known for DtBSe but not for DtBS and the dotted line is an estimation of the VP as provided by the supplier Epichem Ltd.

3.4.5 Literature review

Table 3.2 lists some of the more prominent groups involved in the MOVPE growth of the CuGaS\(_2\) in particular.

<table>
<thead>
<tr>
<th>Author</th>
<th>Material</th>
<th>Precursors</th>
<th>(T_G) (°C)</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hara</td>
<td>CuGaS(_2)</td>
<td>CpCuTEP</td>
<td>TEGa, H(_2)S, DES</td>
<td>600-650</td>
</tr>
<tr>
<td>Honda</td>
<td>CuGaS(_2)</td>
<td>CpCuTEP</td>
<td>TEGa, DtBS</td>
<td>600</td>
</tr>
<tr>
<td>Chichibu</td>
<td>CuGaS(_2)</td>
<td>CpCuTEP</td>
<td>TPGa, DtBS</td>
<td>600</td>
</tr>
</tbody>
</table>
Although each of these groups have published a number of papers covering various aspects of the growth and characterisation of this material, the relatively small number listed in Table 3.2 demonstrates the scarcity of information available. As one can see from this table, no prior studies have involved the MOVPE growth of CuGaS$_2$ using the Cu precursor Cu(hfac)$_2$Et$_3$N or the gallium precursor TMGa in conjunction with CpCuTEP. Of course, there are a number of other studies investigating the growth of other chalcopyrites by MOVPE; however, these will not be discussed in this work.
CHAPTER 4

EXPERIMENTAL TECHNIQUES

There are a number of significant differences in the MOVPE growth of CuGaS$_2$ when compared with the growth of other III-V or II-VI material systems. In addition to these differences, particular techniques were employed in the analysis of the grown epilayers. All relevant information is described in some detail in this chapter.

4.1 Growth technique

Thin films of CuGaS$_2$ were grown in an Epitor 04 laboratory-scale MOVPE crystal growth system (depicted in Fig. 4.1). The volume of purified H$_2$ carrier gas is controlled via electronic mass-flow controllers in order to prevent fluctuations resulting from pressure or flow changes. The system can accommodate up to five metalorganic sources maintained in temperature baths, and four hydride and/or gaseous dopant sources. The flow of carrier-gas through each of these lines is also controlled by electronic mass-flow controllers. Resistive heating tape wrapped around the stainless steel tubing allows the lines to be maintained at particular temperatures in order to prevent unwanted condensation of a precursor within the tubing. A fast-switching manifold permits complicated heterostructures to be grown with abrupt interfaces. For the growth of CuGaS$_2$, however, it was necessary for both the Cu and S precursors to bypass the manifold and be fed separately into the line approximately 10 cm upstream from the reactor tube. This was done to in order to minimize any possible pre-reaction between precursors as well as to prevent contamination in the future growth of other material systems.

The quartz reactor tube includes a water jacket situated on the upper surface. Growth temperatures were reached using an infrared heater situated below the susceptor, and was maintained (using proportional, integrated and differential settings, PID) by a Eurotherm temperature controller. Both the vent and carrier line (after passing through the reactor) are heated by pyrolysis furnaces where the reagents are rendered safe before being
filtered from the carrier gas. Extraction units are situated above the reactor tube, but in a position slightly closer to the reader than that of the reactor itself (see Fig. 4.1). This is known to cause some non-uniform heating and will be discussed further in section 5.1.

![Figure 4.1](image-url)

**Figure 4.1.** Schematic layout of the MOVPE reactor. Heated pipes are represented by dashed lines and the arrows indicate the direction of gas flow.

A typical growth process involves substrate preparation, an anneal phase, and finally growth for a period of between 1 and 4 hours.

### 4.1.1 Substrate preparation

CuGaS$_2$ epilayers were grown on a number of different types of substrates during the course of this study. GaAs substrates orientated in the (001) direction were chosen for the growth of epitaxial CuGaS$_2$. Similar substrates missorientated by 10° toward the (110) plane, were placed alongside the straight (001) substrates during growth for some experiments in order to investigate the effect of misorientation on epitaxy. Growth was simultaneously performed on (001) Si substrates in order to obtain an accurate analysis of the composition by energy dispersive X-ray spectroscopy (EDS). Substrates were provided by EPI Materials Ltd. (UK) and Sumitomo Electrical Industries (Japan). Pieces of the appropriate size (approximately 1.5 x 1.0 cm$^2$) were cleaved from the rear of the substrate using a diamond scriber and blown clean with purified N$_2$. Pieces of 10° off
GaAs substrates (EPI Materials Ltd. (UK)) and larger pieces of (001) Si substrates (also provided by Sumitomo) were prepared in a similar manner. These substrates were mounted on the susceptor in the positions shown in Fig. 4.2.

![Diagram](image)

**Figure 4.2.** Position of substrates during growth. The direction of the carrier gas is as indicated and the thermocouple is embedded half-way along the inside of the susceptor from the rear.

### 4.1.2 Conditions under which precursors are used

This subject was discussed in some detail in chapter 3, however, the conditions under which these precursors were used needs some mention here. As mentioned previously, a number of precursors were used in this study, namely CpCuTEP, TMGa, Cu(hfac)$_2$
Et$_3$N, TEGa and DtBS. However it is the results obtained from the latter three that will be discussed in the greatest detail. To date all MOVPE crystal growth of CuGaS$_2$ has been attempted using CpCuTEP as a copper source (Hara *et al.*, 1998; Siebentritt *et al.*, 2002; Chichibu *et al.*, 1997; Chichibu *et al.*, 1998; Bauknecht *et al.*, 2000a; Shirakata and Chichibu, 2000; Harada *et al.*, 2001; Honda *et al.*, 1993; Artaud-Gillet *et al.*, 2003). No pyrolysis data is available for this molecule, and a solitary VP value of 0.01 Torr at 60 °C is reported by the suppliers (Morton International). As a result, most studies report the introduction of CpCuTEP into the reactor in terms of l/min. It is typical to vary the group III precursor, usually TEGa or normal-tripropylgallium (TPGa), when studying the effect of the group I/III ratio and VI/(I+III) ratio on crystalline quality. Even less data is available for the relatively new copper precursor Cu(hfac)$_2$
Et$_3$N and a VP of 0.25 Torr at 25 °C is estimated for this precursor, based on the VP of the similar metalorganic...
Cu(hfac)$_2$Et$_3$N. The VP of Cu(hfac)$_2$, without the Et$_3$N ligand, is reported to be 0.25 Torr at ~ 62 °C. The purpose of the Et$_3$N ligand is to provide added volatility to the molecule. DtBS has been used extensively for some years now and the semi-log VP curve as a function of bubbler temperature has been discussed in Fig 3.7. VP values of TMGa and TEGa are well known and the values used in this study are listed in Table 4.1 along with data pertaining to the other precursors.

Resistive heating of the stainless steel tubing through which the carrier gas is fed into the copper and sulphur sources was used. The very low VP values of the Cu precursors and the large excess of group VI precursor required for the growth of CuGaS$_2$, necessitates large volumes of carrier to flow through these lines. Failure to heat the carrier gas being fed into the sources may result in the carrier gas cooling on the inside of the bubbler. The piping between the copper and sulphur bottles and the inlet of the reactor tube was also heated to temperatures of between 5 and 10 °C in excess of the bubbler temperatures, to prevent unwanted condensation inside these lines.

Table 4.1
Vapour pressures of the precursors used in this study.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Bath temperature (°C)</th>
<th>Vapour pressure (Torr)</th>
<th>Inlet temp. (°C)</th>
<th>Outlet temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpCuTEP</td>
<td>60</td>
<td>0.01</td>
<td>60</td>
<td>60 - 75</td>
</tr>
<tr>
<td>Cu(hfac)$_2$Et$_3$N*</td>
<td>45 – 57*</td>
<td>0.25</td>
<td>45 - 57</td>
<td>45 - 70</td>
</tr>
<tr>
<td>TMGa</td>
<td>-9</td>
<td>42</td>
<td>-</td>
<td>35**</td>
</tr>
<tr>
<td>TEGa</td>
<td>0</td>
<td>0.80</td>
<td>-</td>
<td>35**</td>
</tr>
<tr>
<td>DtBS</td>
<td>35</td>
<td>8.0</td>
<td>35</td>
<td>35 - 45</td>
</tr>
</tbody>
</table>

*Higher temperature owing to loss of Et$_3$N ligand, ** Heating of manifold

4.1.3 Typical growth conditions

Owing to the large number of variables present in the MOVPE growth process, care must be taken to ensure that identical conditions are employed for each growth run in order to ensure reproducibility. Before starting a growth process, all line heaters, precursor temperature baths and pyrolysis furnaces are maintained at the temperature required during growth for a minimum of thirty minutes before growth is initiated. Thereafter,
substrates are prepared in the manner described in Sect. 4.1.1 and loaded immediately into the quartz reactor.

Figure 4.3. Temperature profile of a typical growth run. Patterned bars represent the flow of each of the four precursors and the stage at which they are introduced and terminated.

The initial stage of growth involves an anneal phase at a temperature of ~750 °C for 10 minutes in order to provide a clean GaAs surface for the growth of CuGaS$_2$. During this phase ~100 sccm of AsH$_3$ are passed through the reactor in order to prevent the loss of As from the surface of the GaAs substrates. The flow of AsH$_3$ is maintained until the introduction of the Cu and Ga precursors at the start of growth. However, the flow of DtBS is introduced into the reactor ~10 seconds before this occurs, in order to ensure that this precursor reaches the susceptor before any other precursor (it is supplied via separate piping). The timing and order in which the precursors were introduced into the reactor were varied for a series of epilayers in order to investigate the effect of this variable on the epitaxial quality of grown layers. These changes are described within the results section of this study. After the completion of the growth stage, there is a cool-down period of ~10 minutes before the layers are removed from the reactor.
4.2 Characterisation techniques

Thin films of CuGaS$_2$ grown by MOVPE were characterised by a number of different techniques in order to obtain as much information pertaining to the structural, compositional and optoelectrical nature of the material as possible. All thin films were analysed by X-ray diffractometry (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). Selected layers were additionally analysed by transmission electron microscopy (TEM), Rutherford backscattered spectroscopy (RBS) and Raman spectroscopy. The fundamental theory concerning each of the techniques mentioned above will be summarized briefly below.

4.2.1 X-ray diffractometry

X-ray diffractometry (XRD) is a particularly powerful non-destructive technique, which allows one to determine the structural properties of grown epilayers, as well as identify any secondary phases present. Crystalline quality can also be assessed based upon the full width at half-maximum (FWHM) of peaks present in XRD spectra. XRD is based upon Bragg’s Law:

$$n \lambda = 2d_{hkl} \sin \theta_{hkl}$$  \hspace{1cm} (4.1)

where $d_{hkl}$ is the spacing between the planes indicated by the Miller indices $(hkl)$, $\theta_{hkl}$ is the acute angle between the incident radiation and the $(hkl)$ planes, $n$ is the order of the reflection, and $\lambda$ is the wavelength of the incident radiation. Since the angle of the incident X-rays equals the angle of the emerging, Bragg-diffracted X-rays, the Geiger counter, that measures the intensity of the diffracted X-rays, is placed at an angle of $2\theta_{hkl}$. The table below lists the relationships between $d_{hkl}$ and the lattice parameters of the unit cells for some of the more common crystal systems, as well as the selection rules stipulating the allowed and disallowed reflections for each of the lattice types.
Table 4.2
Relationship between $d_{hkl}$ and the lattice parameters for each of the basic crystal lattices.

<table>
<thead>
<tr>
<th>System</th>
<th>Bravais lattice</th>
<th>Axial lengths and angles</th>
<th>Relationship</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>Simple</td>
<td>$a = b = c, \alpha = \beta = \gamma = 90^\circ$</td>
<td>All reflections possible $h+k+l = 2n$</td>
<td>$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$</td>
</tr>
<tr>
<td></td>
<td>Body-centred</td>
<td></td>
<td>$h, k, l$ is even or odd</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Face-centred</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Simple</td>
<td>$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$</td>
<td>Depends on Bravais lattice</td>
<td>$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$</td>
</tr>
<tr>
<td></td>
<td>Body-centred</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Simple</td>
<td>$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$</td>
<td>All reflections possible</td>
<td>$\frac{1}{d_{hkl}^2} = \frac{4}{3} \frac{h^2 + k^2 + l^2}{a^2} + \frac{l^2}{c^2}$</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>Simple</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A Philips PW1840 X-ray diffractometer (which gave a resolution of 0.02° 2θ) was used to characterise all layers. CuKα radiation ($\lambda = 1.5402$ Å) was used as a source. Due to inhomogeneities in the composition of thin films, additional XRD measurements were performed on cleaved pieces of the epilayer in order to more accurately attribute phases identified by XRD to particular compositions.

4.2.2 Scanning electron microscopy

Investigations of surface morphology and layer thickness were carried out on the scanning electron microscope (a Philips XL 30 SEM). This device employs the use of electrons instead of light to image the grown epilayers. Since samples are bombarded by a beam of high-energy electrons during analysis, it is vital that they are made conductive in order to prevent charge build-up and possible damage to the surface. In order to make this possible, all samples were prepared in the standard manner and mounted on aluminium stubs, which act as a charge “sink” through which the electrons may drain. Electrons interact with the sample surface, rebound, and are then detected and converted into an image on the computer monitor. Backscattered-electrons, which are more sensitive to elements of different densities, where also employed during the analysis of
cross-sections (when the interface was difficult to see). A beam energy of 20 kV was employed to obtain images, with a variable spot size depending on the degree of magnification employed.

4.2.3 Energy dispersive X-ray spectroscopy

Because of the electron bombardment within the SEM, X-rays of particular energies are generated depending on the elements present within the sampling volume of the electron beam. These energies are interpreted by the EDAX program and a qualitative analysis of the sample is possible. A quantitative analysis of a sample is also possible by comparing the relative ratios of these X-ray energies collected over a particular time period. The use of GaAs as the substrate of choice in this study significantly complicated the quantification process. This was because of a contribution by the Ga within the substrate as well as the epilayer to the overall composition of the sample. An obvious solution to this problem would involve a decrease in the accelerating voltage in order to minimise the excitation volume to a depth smaller than that of the thickness of the epilayer. However, in most cases the epilayers are sub-micron in thickness and/or cover the substrate incompletely. The only solution to this problem involved the simultaneous growth of CuGaS₂ thin films on GaAs(001) and Si(001) substrates as depicted in Fig. 4.2. Compositional analysis was performed on the Si substrates whereas epitaxial growth was investigated for CuGaS₂ deposited on GaAs substrates.

![Diagram](image)

**Figure 4.4.** An estimation of the difference in excitation volumes expected for a 20 kV beam (a) and a 5 kV beam (b).
A 5 kV accelerating voltage was still employed despite using the thin film deposited on the Si substrate as a means for determining the composition of the CuGaS$_2$/GaAs epilayer. The reason for this can simply be explained using the illustrations in Fig. 4.4. By using a smaller accelerating voltage, a smaller excitation volume results, thereby leading to a larger percentage of the epilayer contributing to the overall excitation volume. As a result, a smaller error in the final composition is expected.

An additional problem is encountered through this technique. The energies of the X-rays for each of the elements Cu, Ga and S resulting from both the K and L transitions are given in Table 4.3.

<table>
<thead>
<tr>
<th>Element-transition</th>
<th>Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-L</td>
<td>0.925</td>
</tr>
<tr>
<td>Ga-L</td>
<td>1.095</td>
</tr>
<tr>
<td>Si-K</td>
<td>1.735</td>
</tr>
<tr>
<td>S-K</td>
<td>2.305</td>
</tr>
<tr>
<td>Cu-K</td>
<td>8.035</td>
</tr>
<tr>
<td>Ga-K</td>
<td>9.245</td>
</tr>
</tbody>
</table>

As one can see from Table 4.3, the X-rays resulting from the K transitions in Cu and Ga are too high in energy to be excited by a 5 kV electron beam. As a result, quantification must be done using the sulphur K-transition and the copper and gallium L-transitions instead of the standard method of quantifying by transitions of a particular type only (for example the copper, gallium and sulphur K–transitions). Tests were performed to ascertain the error induced by this method (not included in these results), but the differences were negligible.

4.2.4 Transmission electron microscopy

Cross-sectional samples were prepared in the standard manner, schematically illustrated in Fig. 4.5. Relevant sections of the thin film grown on GaAs substrate were cleaved from the rear along a [110] direction using either a diamond scriber or saw. The dotted
lines and arrows in Fig. 4.5 (a) indicate the cleave planes. A ‘sandwich’ was made by gluing together epilayer surfaces 1 and 2 of Fig. 4.5 (a) and (b) (facing each other) and gluing and additional substrate piece to the outside of pieces 1 and 2 (see Fig. 4.5 (b)). Fig. 4.5 (c) illustrates how; after grinding and polishing approximately half of the structure from the edge; it can be mounted on a copper grid. Polishing is done using pastes with successively smaller particles in suspension (5 µm, 1 µm and then 0.25 µm). After mounting on the copper grid, the same process of grinding and polishing is then submitted to the unpolished side until the structure has been thinned to ~50 µm (seen in Fig. 4.5 (d)). The sample is then loaded into an Ar⁺-mill where it undergoes bombardment by high energy ions (Fig. 4.5 (e)) for a number of hours depending on the thickness, angle of incidence and energy of the incoming ions. This allows the specimen to be thinned to a thickness suitable for TEM analysis.

**Figure 4.5.** Pieces of epilayer (1 and 2) are cleaved using a diamond scriber or saw (a), and glued together with the upper-surfaces facing each other (b). The polished side of the sandwich structure is glued edge-on onto a copper grid before the other side is thinned and polished (c). Once the specimen has been polished to a mirror-like finish and is of the order of ~50 µm thick (d), it is loaded into an ion mill and thinned even further, until a hole is formed in the middle (e).

Planar samples were prepared in a slightly different manner. The relevant pieces were cleaved from the sample and mounted upper-side down on the copper grid. The substrate side was then thinned and polished in the same manner as the cross-sectional sample.
described above. When using the ion mill to thin the specimen to its final thickness, care must be taken to ensure that the beam only mills the substrate side of the specimen (top surface).

Transmission electron microscopy was carried out on a 120 kV Philips EM 420 fitted with an EDAX EDS system. There was considerable uncertainty within the EDS measurements obtained from the TEM due to Ga from within the substrates (which may have been “sputtered” due to the ion-milling process) and Cu from within the TEM grid. EDS measurements were used as a guideline only. Micro-diffraction and selected area diffraction (SAD) patterns were used to determine structure type and lattice parameters of the films. Comparisons were made with simulated diffraction patterns generated by JEMS electron diffraction software (Stadelmann, 1999).

High resolution transmission electron microscopy was carried out at the Humboldt University of Berlin on a JEOL JEM-2200 FS electron microscope using an accelerating voltage of 200 kV.

4.2.5 Photoluminescence spectroscopy

Photoluminescence (PL) spectra were obtained using the 457.9 nm line of an Ar⁺-ion laser as an excitation source. The beam was focused (to a point of ~200 µm) and directed onto the sample by a small mirror. The samples were housed in a closed-cycle helium cryostat capable of obtaining temperatures as low as 4.2 K. The PL emitted by the sample passed through a condenser lens followed by a high pass filter, which removed the reflected laser beam, before being focused onto the entrance slit of a 0.5 m spectrometer. The spectrometer was calibrated using the 632.8 nm line of a He-Ne laser. The signal is detected by a GaAs photomultiplier and amplified by a lock-in amplifier interfaced to a computer. Variable laser power measurements were made using neutral density filters to vary the intensity of the incident laser on the sample. A maximum laser power of 20 mW was used in order to avoid local heating of the sample. Variable
temperature measurements were performed on selected samples between the temperatures of 14 and 298 K.

4.2.6 Raman spectroscopy

Room temperature measurements were performed using a Jobin-Yvon T64000 triple Raman spectrometer that operated in triple subtractive mode. The 514.5 nm line of an Ar⁺-ion laser, was used to excite the samples. The laser beam was focused using a 20x or 50x objective lens, which gave a spot size of ~1.5 µm and ~1.1 µm in diameter respectively. The latter lens offered a better signal to noise ratio. A backscattered configuration of the charge-coupled device (CCD) camera was used to collect an unpolarised Raman signal, and recorded with a Labspec v3.03 software from Jobin-Yvon. All measurements were performed on the region of interest for each sample.

4.2.7 Rutherford backscattering spectroscopy

Rutherford backscattering spectroscopy (RBS) is a fast and direct method for obtaining elemental depth profiles in solids (Ziegler, 1977; Chu et al., 1978) with typical accuracies of a few percent. However, it relies heavily on the need for a thin sample which is (in the ideal case) perfectly smooth and free of any undulations in the surface. The detection limits of this technique range from a few parts per million for the heavier elements to a few percent for the lighter elements. A penetration depth of approximately 2 µm is not uncommon when utilizing He as the probe atom.

The basic principle of Rutherford Backscattering Spectrometry (RBS) lies with the simple kinematics of binary collisions. When a sample is bombarded with a beam of high-energy particles, a small fraction of these particles will undergo a coulombic collision with the nucleus of the sample atom, thereby being “back-scattered” with a lower energy than that of the incident particle. The energy of the back-scattered particle is a function of its own mass $M_1$, the mass $M_2$ of the target atom, and the scattering angle $\theta$ as measured between the original particle trajectory and the trajectory of the scattered...
particle. The ratio of the projectile energy after a collision to the projectile energy before a collision is known as the *kinematic factor*, and is given by:

\[ K = \frac{E_{\text{scattered}}}{E_{\text{incident}}} = \left[ \left( 1 - \left( \frac{M_1 \sin \theta}{M_2} \right)^2 \right)^{1/2} + \frac{M_1 \cos \theta}{M_2} \right]^{2} \left( 1 + \frac{M_1}{M_2} \right) \]

where \( E \) is the ion energy, \( M_1 \) and \( M_2 \) is the mass of the incident ion and target atom respectively, and \( \theta \) is the scattering angle.

When an incident particle strikes an atom with a low mass, a significant amount of its kinetic energy is transferred to the atom. The difference in energy between the incident and backscattered particle is quite large and hence contributions from lighter elements are much easier to resolve. As the target atom increases in mass, the energy of the backscattered particle asymptotically approaches the energy of the beam. Another important consideration when using this technique is that the very light elements such as H or He cannot be detected by the normal RBS geometry. This is due to the incident particle not undergoing a backscattering but rather maintaining its forward momentum after striking the target atom. However, if a detector is so placed as to detect forward-scattered particles then these elements can also be recorded using the same principles as that of RBS. The number of backscattered particles also increases dramatically with an increase in atomic number. This trend is explained in terms of the *scattering cross-section* defined as:

\[
\frac{\partial \sigma}{\partial \Omega} = \left[ \frac{Z_1 Z_2 e^2}{4E} \right]^{2} \cdot \frac{4}{\sin^4 \theta} \cdot \frac{1}{\sqrt{1 - \left( \frac{M_1 \sin \theta}{M_2} \right)^2 + \cos \theta}} \cdot \left[ 1 - \left( \frac{M_1 \sin \theta}{M_2} \right)^2 \right]^{2} \]
\]  

(4.3)
where $Z_1$ and $Z_2$ are the atomic numbers of the incident ion and target atom respectively, $E$ is the energy of the incident ion, and $\theta$ is the incident and scattered angle. It is difficult to determine the identity of heavier atomic species, since the mass resolution decreases with increasing mass. In addition, the peaks attributed to Cu and Ga are relatively difficult to resolve in RBS spectra as both elements have a similar mass.

Only a small fraction of the incident ions are actually backscattered from the target, whereas most end up being implanted into the target material. The stopping power of the target material depends on a number of factors, which include the type of incident ion, its velocity, the elements in the target and the density of the target material. The majority of incident particle energy loss is caused by electron interaction, which is a complicated process. In order to simplify this process (and increase accuracy), any analysis using the RUMP simulation package (Doolittle, 1985) uses the units of atoms/cm$^2$ for the thin film thickness $d$ instead of standard units. For CuGaS$_2$, the relationship in Eq. 4.4 can be obtained considering the lattice parameters of $a = 5.360$ Å, $c = 10.488$ Å and 16 atoms per unit cell:

$$d_{\text{actual}} \ (\text{cm}) = \frac{d_{\text{RBS}} \ (\text{atoms} / \text{cm}^2)}{5.31 \times 10^{22} \ \text{atoms} / \text{cm}^3}$$

(4.4)

where the actual thickness, $d_{\text{actual}}$ is given in cm, the RBS thickness, $d_{\text{RBS}}$ is given in atoms/cm$^2$, and the density of atoms in CuGaS$_2$ has been calculated to be $5.31 \times 10^{22}$ atoms/cm$^3$.

RBS can also be used to analyse the structure of epitaxial thin films. When the rows of atoms of a single crystalline sample are orientated parallel to the particle beam, the condition is set for channeling to occur. When this takes place, the incoming beam will experience a backscattering effect off the first few monolayers of the sample to approximately the same degree as that for a non-aligned sample. However, when the beam penetrates further into the material, significantly less interaction occurs between the
beam particle and the target atoms owing to the shielding effect of the inner atoms by the overlying atoms. The channeling effect allows one to quantify the degree of epitaxy present for a particular thin film.

Analysis was performed using a 2 MeV beam of He$^+$ particles with a phi/theta configuration of 15 and -10 degrees respectively. Reference samples were used to calibrate the system and obtain the correct channels for the respective elements. Simulations were performed using the RUMP RBS simulation software detailed by Doolittle (1985).
CHAPTER 5

COMPOSITION AND SURFACE MORPHOLOGY

The physical properties of CuGaS$_2$ epilayers can be influenced by the type and concentration of intrinsic defects introduced through deviations from stoichiometry. In this chapter, changes to the composition and surface morphology of the grown layers are investigated as a function of the changing growth parameters.

5.1 Non-uniformity of epilayer composition and surface morphology

There are a number of factors which can affect the uniformity of grown epilayers, of which temperature, reactor design, carrier-gas flow and the type of MO precursor are some of the more commonly known. Any pre-reaction, which may occur between precursors, will cause significant depletion of the species in the direction of the carrier gas flow.

In section 4.1 a description was given of the separate inlets through which the copper and sulphur precursors are fed into the reactor. All three metalorganics (including TEGa) are combined at a three-way junction, which may cause some separation of the precursors for a short region downstream from this point. A comparatively large distance is traversed between this junction and the heated region of the reactor (~15 cm) and complete mixing is assumed to have occurred before the carrier gas has reached the leading edge of the susceptor.

A description was given in section 3.3.2 of the temperature profile present within the reactor tube. This profile is magnified when cooling water is passed through the cooling jacket situated on the upper surface of the reactor tube. The temperature profile described in section 3.3.2, however, can only exist in the ideal case, and it is more likely that temperature non-uniformities occur. It has been found (Ehlers, 1989) that in the current reactor a distinct asymmetric temperature profile exists, resulting from cooling effects
due to the reactor cabinet ventilation (see section 4.1). This temperature profile is shown in Fig. 5.1. It was shown in section 3.3.2 that a lower temperature is expected at the leading edge of the susceptor, however, the parabolic nature of this profile toward the rear of the susceptor is unusual. The highest temperatures are experienced downstream toward the “rear” of the reactor. The lowest temperatures occur toward the “front” of the reactor, nearer to the leading edge. As a result the temperature can vary by as much as 80 °C across different regions of the susceptor surface.

Figure 5.1. Temperature profile of the susceptor surface for a total He gas flow of 4.5 l/min, heated from below by IR radiation to a temperature of 975 K (Ehlers et al., 1989).

To investigate the effect that non-uniform heating or reactor design may have on thin film uniformity, a single thin film of CuGaS$_2$ was deposited on a Si(001) substrate at a growth temperature of 600 °C for a period of 2 hours. The I/III and VI/(I+III) ratios in the vapour phase were 28.2 and 12.1 respectively and a total H$_2$ flow of 4.95 l/min was used. The substrate covered the entire susceptor surface (20x25 mm$^2$). The resulting layer was analysed by EDS and a three-dimensional (3D) profile of the solid content of each of the elements Cu, Ga and S is plotted as a function of position on the substrate surface in Fig. 5.2 (a)-(c) respectively. To understand these composition profiles it is necessary to assume that Cu is the minority species in the system and that a parasitic reaction between the Cu and S precursors occurs in the gaseous phase. These speculations will be validated later in sections 5.2.1 and 5.2.2.
Figure 5.2. Compositional profiles of each element in the solid phase, namely copper (a), gallium (b) and sulphur (c) as a function of the position on the susceptor during growth.
From Fig. 5.2 (a) there is a clear drop in the Cu content of the solid from the leading edge to the trailing edge of the substrate. This is expected for the limiting species of a system (see section 3.3.3 regarding concentration profiles within the reactor). TEGa is said to be completely pyrolysed at temperatures in excess of ~350 °C (Stringfellow, 1989, pp. 167). Similarly, Cu(hfac)$_2$Et$_3$N has been used successfully at growth temperatures as low as 400 °C (Artaud-Gillet et al., 2003), at which it is also considered to be completely pyrolysed. Therefore, the increase in the Ga content toward the rear of the reactor cannot be explained in terms of increased cracking efficiency at higher temperatures. Instead, it is likely that the Ga content compensates for the drop in Cu in the direction of the carrier gas flow. Sulphur is known to be extremely volatile at the growth temperatures used in this study (i.e. 550 °C - 600 °C) and a large over-pressure of the group VI species is required when growing the chalcopyrites by MOVPE or MBE. Hence, it is not surprising to measure an increased S-content in the region where the temperature is the lowest (see minima of the parabolic temperature profile). This theory will be confirmed later in this chapter (section 5.2.3), when an increase in growth temperature caused a drastic reduction in the S-content of the grown epilayer.

The non-uniform composition across an epilayer leads to a change in the surface morphology of different regions. Fig. 5.3 illustrates this result particularly well. This epilayer was grown using Cu(hfac)$_2$Et$_3$N, TMGa and DtBS as precursors, at a substrate temperature of 550 °C, a total H$_2$ flow of ~5 l/min and I/III and VI/(I+III) ratios in the vapour phase of 14.9 and 11.8 respectively. This epilayer was simultaneously grown on a Si substrate, placed next to regions 1-3 in the schematic in Fig. 5.3. The compositions of these three regions were estimated using the compositions obtained from neighbouring positions on the Si substrate. The composition of region 1 (which will be taken as the standard region of interest for all subsequent analyses) is significantly Cu-rich (Cu: 27.9, Ga: 21.6 and S: 50.5), but becomes more stoichiometric in region 3 (Cu: 26.2, Ga: 25.0 and S: 48.8). Although these values are relatively similar and arguably within experimental error for EDS analysis, areas further downstream (regions 3, 6 and 8), and toward the centre of the susceptor (regions 1, 2 and 3), are consistently less Cu-rich than other regions. Regions closer to the inlet of the reactor (regions 1, 4 and 7) exhibit
crystallites with a faceted, triangular-based pyramidal appearance as opposed to more-rounded crystallites occurring in regions closer to the vent (regions 3, 6 and 8). This would suggest that crystallites containing less Cu result in a rounding of the surface crystallite present on the thin film surface. It must be noted that this particular thin film was grown using TMGa as a group III precursor. More important, however, was that this film was grown using Cu(hfac)$_2$Et$_3$N before a significant drop in its VP was measured (see section 3.4.2.2).

Figure 5.3. SEM micrographs of identical magnification from the regions indicated on the schematic showing how the surface morphology can change over the substrate surface. The film was grown at a substrate temperature of 550 °C using the precursors: Cu(hfac)$_2$Et$_3$N, TMGa and DtBS over a period of 2 hours with an I/III and VI/(I+III) ratios in the vapour phase of 14.9 and 11.8 respectively. The substrate size is approximately 1 cm x 1 cm in area and the carrier gas flow direction is from left to right. The marker indicates 2 μm.
Due to the non-uniformities described above, all subsequent results (unless mentioned otherwise) are related to regions on the GaAs substrate that are equivalent to region 1 in Fig. 5.3. Care was taken to ensure that all substrates during growth were positioned correctly on the susceptor to ensure that results from different growth runs are comparable.

5.2 Effect of changing growth parameters on composition and surface morphology

Most growth related studies of the chalcopyrites involve the polycrystalline growth of thin films by a variety of techniques (Artaud-Gillet et al., 2003; Hu et al., 2002; Guillén and Herrero, 2002; Orsal et al., 2000; Miyake et al., 1995; Gossla et al., 1995). Less detail is to be found relating the surface morphology as a function of epilayer composition for single-crystalline material grown by MOVPE. It is well known that growth of material under Cu-rich conditions promotes the formation of near-stoichiometric material in addition to binary phases of the group I and group VI elements (Alvarez-García et al., 2001; Aggour et al., 2002; Gossla et al., 1995; Metzner et al., 2000). These binary phases are then removed by submitting the films to a potassium cyanide etch subsequent to growth. This technique is normally used in the polycrystalline growth of the chalcopyrites. Of particular relevance to this study is how growth under Cu-rich conditions can affect the degree of epitaxy for MOVPE-grown material. To investigate this trend, a number of epilayers were grown with varying group I/III and group VI/(I+III) ratios in the gaseous phase, and a comparison made of the composition and surface morphologies of respective layers. These results will be presented in the following section.

5.2.1 Variable I/III in the vapour phase

Fig. 5.4 (a-c) demonstrates the variation in composition across the substrate surface for four epilayers grown with increasing I/III ratio in the vapour phase. The vertical axes for each of the plots (a-c) cover the same scale (6 at. %) for comparative purposes. The I/III
ratio was changed by decreasing the flow of TEGa through the reactor. This was due to the already large flow of carrier gas (~2.5 l/min) delivered to the Cu(hfac)$_2$Et$_3$N bubbler. The VI/(I+III) ratio was maintained at 9.0. Other relevant growth parameters are indicated in Fig. 5.4(c). Note the decrease in Cu content between the leading edge (reactor inlet side) and trailing edge of the sample, whilst the Ga and S content increase. This trend is observed despite the large I/III ratios in the vapour phase and is indicative of Cu as the minority species. The corresponding increase in the Ga and S content is expected if those species are in excess, and is tentatively ascribed to the formation of ordered-defect compounds (ODC’s) such as CuGa$_3$S$_5$ and CuGa$_5$S$_8$, as well as secondary Ga$_x$Sy phases (Chen, et al., 1997) towards the trailing edge of the layer. There is a tendency for a larger rate of decrease in Cu across the epilayer with increase in TEGa, which cannot be explained only in terms of Cu being the minority species. If one considers a pre-reaction between the Cu and Ga metalorganics, then a larger TEGa flow would result in an increase in this pre-reaction. A higher rate of depletion of the minority species (i.e. Cu) would then occur along the gas flow direction.

Fig. 5.4. Composition profiles for copper (a), gallium (b), and sulphur (c) as measured from the leading edge of the substrate for epilayers grown with different I/III ratios (by changing the group III flow rate), namely 37 (■), 42 (○), 47 (▲) and 60 (∇). The values corresponding to the standardised region of interest are circled in each of the figures.

The dependence of the Cu/Ga ratio in the solid phase (for the standardised region of interest) on the TEGa flow rate is depicted as the solid squares in Fig. 5.5. Despite a relatively large increase in the I/III ratio from 37 to 60, all epilayers were identified as
Ga-rich by EDS. One can also deduce from this graph that at sufficiently high flows of the group III precursor (i.e. small I/III ratio in the vapour phase), the ratio of cations in the solid remains largely unaffected by any change in the I/III ratio in the gas phase. A similar study was done by Chichibu et al. (1995) using normal-tripropylgallium (TPGa), CpCuTEP and DtBS. Results from that study (open, grey squares) are depicted alongside the results obtained in this work for comparative purposes. It is evident that for high TPGa flow rates, the results are analogous. In the present study, results were not obtained using TEGa flow rates lower than 0.34 µmol/min (owing to mass flow considerations), and it can only be speculated that a similar trend would be observed to that reported by Chichibu et al. (1995).

**Figure 5.5.** The Cu/Ga ratio in the solid phase as a function of the group III precursor flow rate (solid squares). Results from Chichibu et al. (1995) are depicted as open, grey squares.

Further experiments were performed to investigate the uniformity of the composition and morphology of grown epilayers as a function of the I/III ratio in the vapour phase by varying the Cu(hfac)$_2$-Et$_3$N molar flow rate instead of the TEGa molar flow rate. Fig. 5.6 compares the percentage change in the Cu/Ga ratio in the solid with the percentage change in each of the group I and group III precursor molar flows. From this graph it can
be noted that the composition of the solid is influenced more by changing the Cu(hfac)$_2$·Et$_3$N flow (solid squares) than by changing the TEGa flow (open circles). Samples grown in order to investigate the effect of changing the TEGa flow, were grown at a substrate temperature of 550°C, whilst those samples used for investigating the effect of changing Cu(hfac)$_2$·Et$_3$N flow were grown at a substrate temperature of 600°C. It is believed that the difference in growth temperatures does not affect these results owing to the complete pyrolysis of all three precursors at temperatures below 550°C.

![Figure 5.6](image)

**Figure 5.6.** Percentage change in the Cu/Ga ratio in the solid as a function of the percentage change of TEGa flow (open circles) or Cu(hfac)$_2$·Et$_3$ flow (solid squares), with respect to a reference layer grown using a flow of 0.54 µmol/min and 20.2 µmol/min for the Ga and Cu precursors respectively.

The surface morphologies of the region of interest for each of the layers detailed in Fig. 5.4 are illustrated in Fig. 5.7 for growth on both Si (a-d) and GaAs substrates (e-h). It is clear that the surface morphology of thin films deposited on the silicon substrates varies little with an increase in I/III ratio in the vapour phase. An almost identical morphology was observed in regions extending to almost 15 mm further from the leading edge, where compositions were markedly different (the Cu solid content decreased from ~22 at.% to
~19 at.%). The morphologies of films deposited on the GaAs, however, do vary. At first glance it would appear that no clear trend can be observed between an increase in the I/III ratio in the vapour phase and the resulting morphology.

![Figure 5.7](image)

**Figure 5.7.** SEM micrographs of thin films grown at 550 °C on Si (a-d) and GaAs substrates (e-h). The total carrier gas flow was ~5 l/min and the VI/(I+III) ratio was 9.0. The I/III ratios in the vapour phase and Cu/Ga ratios in the solid are given in the centre of the figure. The marker indicates 2 µm.
However, a comparison of the compositions of these layers (Fig. 5.4) with the morphologies in Figs. 5.7 (e-h), points to a transition in the morphology from relatively smooth and featureless to the formation of larger surface crystallites at a measured Cu/Ga ratio in the solid of ~0.82-0.85. This transition is typical for samples changing from Ga-rich to Cu-rich. The formation of secondary Cu\textsubscript{$x$}S\textsubscript{$y$} phases on the sample surface has been reported by a number of groups for Cu-rich material (Alvarez-García et al., 2001; Aggour et al., 2002; Gossla et al., 1995; Metzner et al., 2000). The Cu/Ga ratio < 1 at which this transition appears to occur in this study is likely related to the method whereby the composition was obtained (see section 4.2.3). The significance of this result in subsequent studies will become apparent.

5.2.2 Variable VI/(I+III) in the vapour phase

Fig. 5.8 demonstrates the variation in composition across the substrate surface for three epilayers grown with increasing VI/(I+III) ratio in the vapour phase. Ratios were changed by increasing the DtBS flow through the reactor. The I/III ratio was maintained at 28.2. More detailed growth parameters are included in Fig. 5.8(c). As described previously, the drop in the Cu content of the solid across the epilayer can be ascribed to the decreased availability of the minority species. For low VI/(I+III) ratios, the drop of ~1-2 at.% in the Cu content over a distance of 10 mm from the leading edge is comparable to that observed in Fig. 5.4. For a higher VI/(I+III) ratio of 12.1, a significant reduction in the Cu content at the leading edge of the epilayer (from ~23 at.% to ~16 at.%) is observed. In addition, the rate at which the Cu is depleted across the epilayer surface is seen to increase. Overall, a drop of ~6 at.% in the Cu content is observed from the leading edge to trailing edge of the layer grown with a VI/(I+III) ratio of 12.1, significantly larger than that observed for lower VI/(I+III) ratios. This increased rate of change in composition can be explained in terms of a pre-reaction also existing between Cu(hfac)\textsubscript{2}Et\textsubscript{3}N and DtBS. As the Cu is depleted in the direction of the carrier gas flow, the tendency to form secondary Ga\textsubscript{$x$}S\textsubscript{$y$} phases and ODC’s would be increased, which might explain the increase in Ga and S content toward the trailing edge of the epilayer (Fig. 5.8(b) and Fig. 5.8(c), respectively).
Figure 5.8. Composition profiles for copper (a), gallium (b), and sulphur (c) as measured from the leading edge of the substrate for three epilayers grown with different VI/(I+III) ratios, namely 7.07 (■), 9.54 (○) and 12.1 (▲). The values corresponding to the region of interest are circled in each of the figures.

It is well known that in order to grow epitaxial CuGaS$_2$ by MOVPE, an excess of the group VI species is required. This detail is similar to the growth of the III-V compounds where an excess of the group V species is required.

In Fig. 5.9, the S/Cu ratio in the solid phase has been plotted as a function of the DtBS flow rate (and hence variable S/(Cu+Ga) ratio) alongside similar results reported by Chichibu $et$ $al.$ (1995). In that study, a saturation of the S/Cu ratio in the solid was measured for an increase in the DtBS flow rate beyond a value of ~800 µmol/min. A similar trend should be observed in our work for similar molar flow rates of the group I and group III precursors. However, in the present work, significantly higher molar flow rates were used for the group I and group III precursors. Consequently, sufficiently high DtBS flow rates were not used in this study to obtain a saturation of the S/Cu ratio in the solid. A number of other factors may also contribute to the differences observed between the two sets of results. Chichibu $et$ $al.$ (1995) used normal-tripropylgallium as a group III precursor. In addition to this, a growth temperature of 600 ºC was used, which may have been a limiting factor in the degree to which S was incorporated into the CuGaS$_2$ crystal lattice.
This work
Chichibu (1995)

This work: $T_g = 550 ^\circ C$
$t_g = 2$ hours
$I/III = 28.2$
Total $H_2 = 5 \text{ l/min}$

Figure 5.9  The influence of the VI/(I+III) ratio on the S/Cu ratio in the solid phase. Solid squares represent results from this present work, whilst open squares represent values reported by Chichibu et al. (1995) for growth at 600 °C.

The surface morphology of the same layers detailed in Figs. 5.8 are presented as a function of the VI/(I+III) ratio in the vapour phase in Fig. 5.10. Figs. 5.10 (a-c) represent those layers grown on Si(001) substrates, whilst Figs. 5.10 (d-f) represent those layers grown simultaneously on GaAs(001) substrates. It was consistently found that the thin films deposited on Si substrates were characterised by smaller crystallites with a more uniform distribution than the thin films deposited simultaneously on GaAs substrates. This result is not unexpected: epitaxial growth on unetched, Si(001) substrates is highly unlikely due to the presence of the stable oxide, and polycrystalline growth of CuGaS$_2$ is anticipated. However, an increase in the VI/(I+III) ratio in the vapour phase resulted in a decrease in the size of the surface crystallites for layers on both substrates. The SEM micrographs of the two thin films deposited on GaAs at lower VI/(I+III) ratios displayed densely packed surface crystallites suggesting polycrystalline growth of CuGaS$_2$ and/or secondary phases.
Figure 5.10. SEM micrographs of thin films grown at 550 °C on Si (a-c) and GaAs substrates (d-f). The total carrier gas flow was ~5 l/min and the I/III ratio was 28.2. The values for the VI/(I+III) ratio in the vapour phase are given down the centre of the figure. The marker indicates 2 μm.

XRD spectra of these two samples indeed indicated polycrystalline growth (not shown here), deduced from the dominance of the 112 peak. The compositions of both samples are close to that at which the surface morphology was observed to change from a smooth surface to one dominated by surface features (at a measured Cu/Ga ratio of ~0.82-0.85 - see section 5.3.1). The sample grown at a VI/(I+III) ratio of 12.1 is severely Ga-rich (I/III ratio of 0.5) and as a result the formation of secondary Cu₃S₇ phases is unlikely. The XRD spectrum of this sample indicated c-axis orientated epitaxial growth (not shown here), deduced from the dominance of the 004 and 008 peaks. It is clear from the above
results that a change in the Cu/Ga ratio of the solid strongly influences the surface morphology of the grown thin films.

5.2.3 Variable growth temperature

Fig. 5.11 shows the effect of substrate temperature on the amount of Cu, Ga or S incorporated into the solid at different positions along the substrate surface. The total carrier gas flow was 4.95 l/min and the I/III and VI/(I+III) ratios were 28.2 and 7.07 respectively.

![Composition profiles](image)

**Figure 5.11.** Composition profiles for each of the elements, copper (a), gallium (b), and sulphur (c) as a function of distance from the leading edge of the substrate for three epilayers grown at different growth temperatures, namely 550 °C (■), 575 °C (○) and 600 °C (▲). Lines are a guide to the eye.

From Fig. 5.11 (a) it appears that an increase in growth temperature results in an increase in the copper incorporation. This result has been confirmed from other experiments. With the exception of the first measurement closest to the leading edge, the Ga content remains relatively unaffected by a change in temperature (see Fig. 5.11 (b)). However, it appears that the S content decreases slightly with an increase in growth temperature, while the Cu content increases. The high overpressure of S required for the successful MOVPE growth of CuGaS$_2$ is due to the low sticking-coefficient of this species at typical growth temperatures. A further increase in the substrate temperature will consequently exacerbate this problem and result in a decreased availability of S on the growth surface.
The reason for the increased incorporation of Cu as opposed to an increase in the Ga incorporation is less clear. The TEGa MO is completely pyrolysed at 550 °C (Pütz et al., 1986) and the number of species available for the growth of CuGaS₂ is unaffected at higher temperatures. However, it may be speculated that sufficient S at the growth front is required for the effective incorporation of Cu into the lattice of CuGaS₂. Less S is available for higher substrate temperatures, and as a result there is a tendency for Cu to agglomerate on the surface instead of being incorporated into the CuGaS₂ lattice.

**Figure 5.12.** SEM micrographs of three thin films grown at various temperatures, T_G, on Si (a-c) and GaAs substrates (d-f). The I/III and VI/(I+III) ratios in the vapour phase are 28.2 and 7.07 respectively. A total H₂ flow of 4.95 l/min was used. The marker indicates 5 µm.
The surface morphology of the same layers discussed in Fig. 5.11 is presented as a function of the growth temperature, $T_G$ in Fig. 5.12. Little change is observed in the surface morphology of thin films deposited on Si substrates with a change in growth temperature. The thin films deposited on the GaAs(001) substrates are characterised by a denser packing of larger surface crystallites at lower temperatures. The similarity in composition between the samples grown at 550 °C and 575 °C suggest that the crystallites observed for each of these layers are of the same phase. According to the XRD spectra (not shown here), the layer is 112 orientated CuGaS$_2$). The XRD spectrum of the sample grown at 600 °C (not shown here) exhibited no peaks other than that of the substrate. Some confusion may arise as to why there is clearly some degree of deposition on the substrate surface yet analysis by XRD is unable to identify which phase(s) is responsible.

![Figure 5.13](image)

**Figure 5.13.** EDS mapping of the layer grown on GaAs at a temperature of 600 °C (see also Fig. 5.12 (f)). A 5 kV image of the sample (a) illustrates the position of a larger crystallite, whereas the distribution of Cu (b), Ga (c) and S (d) are given in yellow, green and red respectively. The marker indicates 5 µm.
A means for identifying the composition of the crystallites is to perform an elemental map of the sample surface by EDS. Fig. 5.13 illustrates the distribution of the three elements Cu, Ga and S in the standard region of interest of the sample grown at 600 °C (see also Fig. 5.12 (f)). Measurements were performed using a 5 kV electron beam in an attempt to minimise contribution from the GaAs substrate. From the distribution of elements it would appear that the crystallites are predominantly composed of Cu with a small proportion of S. This corroborates well with the suggestion made earlier that Cu agglomerates on the surface in the event of insufficient S present at the growth interface. Ga is clearly not present in these features and the large distribution prevalent elsewhere on the sample is due to both the Ga deposited during growth and the Ga from the substrate. S is sparsely distributed confirming the enhanced loss of this species at elevated growth temperatures. Chichibu et al. (1995) reported that for the low pressure MOVPE growth of CuGaS$_2$, an increase in the group I precursor flow rate resulted in a decrease in the overall growth rate of the epilayer, which was accompanied by an increased Cu content of the solid. In this work, a decrease in the overall thickness of the layers was also observed with an increase in the growth temperature.

5.2.4 Variable carrier gas flow

Fig. 5.14 illustrates the effect of the total carrier gas flow on the rate of change in composition across the sample surface. Two epilayers were grown with identical precursor mole fractions and substrate temperatures (illustrated in the figure), but for different total H$_2$ flows of 2.48 l/min and 4.95 l/min respectively. It is clear that the total carrier gas flow has an effect on the composition of the final epilayer. The sample grown with the lower total H$_2$ flow displays a decrease in the Cu-content (~4 at.%) and increase in the Ga-content (~3 at.%) for the standard region of interest compared to the sample grown with a total H$_2$ flow of 4.95 l/min. In addition to the drop in Cu for the region of interest alone, the rate of change in composition in the gas flow direction is enhanced for lower flows. It is well known that low-pressure MOVPE growth of the I-III-VI$_2$ semiconductors promotes the formation of a uniform surface morphology and composition. This is especially true when pre-reactions occur between precursors.
Figure 5.14. Composition profiles for each of the elements, copper (a), gallium (b), and sulphur (c) as a function of distance from the leading edge of the substrate for two epilayers grown with different carrier gas flow rates, namely 2.48 l/min (■) and 4.95 l/min (○). An increase in the total carrier gas flow has the effect of thinning the boundary layer in much the same way as in the low-pressure MOVPE growth process. It was shown in section 5.2.2 that a pre-reaction between the Cu and S precursors is likely. An increase in carrier gas flow from 2.48 l/min to 4.95 l/min will cause a thinning of the boundary layer in which this pre-reaction almost certainly occurs, and therefore result in a decrease in the rate of depletion of the minority species (i.e. Cu).

Figure 5.15. SEM micrographs of two thin films grown GaAs substrates with different total H₂ flows of 2.48 l/min (a) and 4.95 l/min (b). The I/III and VI/(I+III) ratios in the vapour phase are 15.0 and 5.6 respectively, and a growth temperature of 550 °C was used. The marker indicates 10 µm.

The surface morphologies of those layers grown on GaAs and discussed in Fig. 5.14 are given in Fig. 5.15. The composition of the layer grown with a total H₂ flow of 4.95 l/min
is close to stoichiometric and the XRD (not shown here) suggests $c$-axis orientated epitaxial growth. It will be shown by TEM in chapter 6 that surface crystallites can indeed be epitaxial in nature and it is possible that these larger crystallites (see Fig. 5.14 (b)) give rise to the peaks observed in the XRD spectra. A halving of the total $\text{H}_2$ flow gave rise to a severe drop in the Cu content of the solid. This in turn resulted in a far smoother surface morphology typical for Ga-rich epilayers (see Fig. 5.15 (a)).

5.3 Rutherford backscattering spectroscopy

RBS spectra were analysed with the aid of the RUMP simulation package (Doolittle, 1985) in order to obtain a comparison with composition profiles of thin films of CuGaS$_2$ obtained from the more commonly used method in this study (i.e. EDS). However, the quantitative analysis of any thin film by RBS is limited to laterally homogenous and smooth surfaces. The work by Metzner et al. (1997, 1998) describes the effect of surface roughness on the RBS analysis of thin films at normal incidence. In this study the FUZZ command in the RUMP simulation package was used to approximate the surface roughness of a representative CuGaS$_2$ thin film. Fig. 5.16 (a) represents the expected spectrum (random noise has been included) for a perfectly smooth CuGaS$_2$ thin film, exactly 0.1 $\mu$m thick, and deposited on a Si substrate. A stoichiometric composition has been chosen for the film (25 at.% Cu, 25 at.% Ga, 50 at.% S). In this spectrum the Cu, Ga and S contributions to the overall signal (black line) are represented by the blue, red and yellow peaks respectively. The broad band at lower energies (and continuing off-scale) is attributed to the Si substrate. For thin films, maxima of the contributions from the Cu and Ga are separately distinguished with the higher energy peak attributed to Ga owing to the larger atomic mass of this element. In Fig. 5.16 (b) an identical thin film has been simulated to adopt an uneven surface morphology by employing a FUZZ function (250 in 10 steps) in the RUMP program. A number of changes to the spectrum are observed when altering the properties of the thin film surface in this way. Firstly, a low-energy tail develops for each of the elemental contributions thereby imparting a low energy tail to the overall spectrum. In the case of an uneven surface, variations in the thickness of the layer impart a range of energies to the backscattered $\alpha$-particles.
Secondly, due to this low-energy tail, the maxima for each of the Cu and Ga contributions can no longer be separated, making an accurate quantification of the layer all the more difficult. In addition to these changes, a small percentage of particles having backscattered off the Si substrate in regions where the film was thinner, now have a higher energy. This effect leads to a slope forming on the higher energy side of the substrate response. In Fig. 5.16 (c) and (d) these effects are more pronounced as the surface is made to appear rougher by doubling the FUZZ factor (500 and 1000 in 10 steps). In the final spectrum, the contribution by the S and the Si substrate are beginning to merge to the point of being almost indistinguishable from one another.

**Figure 5.16.** RUMP simulations depicting the effect of varying surface roughness on a thin film of CuGaS$_2$ with a maximum thickness of 0.1 µm. The spectrum for a perfectly smooth surface is depicted in (a), whereas the surface roughness is doubled for each of the subsequent spectra (b-d).
Fig. 5.16 (d) is obviously an extreme case of variation in film thickness, however, it shall be shown that this is indeed the experimentally observed case in the present study. Fig. 5.17 combines the experimentally obtained spectra for a number of regions across the surface of a thin film of CuGaS$_2$ deposited at 550 °C on a Si substrate. The precursors: Cu(hfac)$_2$-Et$_3$N, TMGa and DtBS were used with a I/III and VI/(I+III) ratio in the vapour phase of 14 and 12 respectively. Fig. 5.17 (a) represents the spectrum obtained for a region ~1 mm from the leading edge of the substrate. Each of the subsequent spectra (Fig. 5.17 (b-g)) correspond to a region a further 1 mm from the leading edge (up to ~7 mm). Each spectrum has been simulated using the PERT function in the RUMP program. For this function, multiple variables were chosen with a minimum and maximum value as indicated in Table 5.1.

### Table 5.1. Starting variables and their minimum and maximum values.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Starting value</th>
<th>Minimum value</th>
<th>Maximum value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface layer thickness [µm]</td>
<td>0.23</td>
<td>0.04</td>
<td>0.38</td>
</tr>
<tr>
<td>Cu in surface layer [at.%]</td>
<td>25</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>Ga in surface layer [at.%]</td>
<td>25</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>S in surface layer [at.%]</td>
<td>50</td>
<td>10</td>
<td>70</td>
</tr>
<tr>
<td>Fuzz of surface layer</td>
<td>1200</td>
<td>0</td>
<td>2000</td>
</tr>
<tr>
<td>Intermediate layer thickness [µm]</td>
<td>0.23</td>
<td>0.04</td>
<td>0.38</td>
</tr>
<tr>
<td>Cu in intermediate layer [at.%]</td>
<td>25</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>Ga in intermediate layer [at.%]</td>
<td>25</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>S in intermediate layer [at.%]</td>
<td>50</td>
<td>10</td>
<td>70</td>
</tr>
<tr>
<td>Fuzz of intermediate layer</td>
<td>1200</td>
<td>0</td>
<td>2000</td>
</tr>
</tbody>
</table>

The fit for each of these spectra is illustrated by the solid line, whereas the contributions from each of the elements are highlighted in blue, red, yellow and green for Cu, Ga, S and Si respectively. Table 5.2 combines the results obtained for each of the simulations. In order to correctly simulate the experimental spectra, it was essential to stipulate a two-layer system, whereby a rough, surface layer overlies a more uniform underlying layer. This criterion is supported by cross-sectional SEM analysis (see Fig. 5.18) from which one can clearly see this feature.
Figure 5.17. Experimental spectra obtained ~1 mm apart starting from a position ~1 mm from the leading edge (a) and tending further toward the trailing edge (b-g) for a layer grown at 550 °C on a Si substrate. Simulations were performed using the PERT function in the RUMP simulation package. Values obtained for these simulations are depicted in Table 2.

Table 5.2. Fitting parameters for each of the spectra in Fig. 5.17. Fitting was performed using the PERT function in the RUMP simulation package starting with the values indicated in Table 5.1.

<table>
<thead>
<tr>
<th>Distance [mm]</th>
<th>Layer</th>
<th>Thickness [µm]</th>
<th>Composition [at.%]</th>
<th>Fuzz</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>upper</td>
<td>0.33</td>
<td>Cu 37 Ga 14 S 49</td>
<td>1080</td>
</tr>
<tr>
<td></td>
<td>lower</td>
<td>0.25</td>
<td>Cu 23 Ga 24 S 53</td>
<td>172</td>
</tr>
<tr>
<td>2</td>
<td>upper</td>
<td>0.25</td>
<td>Cu 32 Ga 15 S 53</td>
<td>1463</td>
</tr>
<tr>
<td></td>
<td>lower</td>
<td>0.28</td>
<td>Cu 17 Ga 30 S 53</td>
<td>248</td>
</tr>
<tr>
<td>3</td>
<td>upper</td>
<td>0.21</td>
<td>Cu 34 Ga 15 S 51</td>
<td>1145</td>
</tr>
<tr>
<td></td>
<td>lower</td>
<td>0.26</td>
<td>Cu 24 Ga 23 S 53</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>upper</td>
<td>0.22</td>
<td>Cu 35 Ga 16 S 49</td>
<td>1177</td>
</tr>
<tr>
<td></td>
<td>lower</td>
<td>0.22</td>
<td>Cu 32 Ga 12 S 56</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>upper</td>
<td>0.20</td>
<td>Cu 33 Ga 17 S 50</td>
<td>1202</td>
</tr>
<tr>
<td></td>
<td>lower</td>
<td>0.20</td>
<td>Cu 35 Ga 11 S 54</td>
<td>105</td>
</tr>
<tr>
<td>6</td>
<td>upper</td>
<td>0.18</td>
<td>Cu 36 Ga 14 S 50</td>
<td>1334</td>
</tr>
<tr>
<td></td>
<td>lower</td>
<td>0.15</td>
<td>Cu 20 Ga 24 S 56</td>
<td>40</td>
</tr>
<tr>
<td>7</td>
<td>upper</td>
<td>0.16</td>
<td>Cu 37 Ga 12 S 51</td>
<td>1310</td>
</tr>
<tr>
<td></td>
<td>lower</td>
<td>0.13</td>
<td>Cu 15 Ga 32 S 53</td>
<td>65</td>
</tr>
</tbody>
</table>
In order to maintain consistency, the minimum, maximum and starting values for each of the variables were identical before the simulations were commenced. These variables included the thickness of both the surface and underlying layer, the relative quantities of Cu, Ga and S in each of the layers, and the degree of surface roughness for each layer. For each of the spectra in Fig. 5.17 (a-g) a good fit was obtained. It is clear from the significant low-energy tail present in each of the spectra that there is a high degree of surface roughness. This is likely to decrease the accuracy of the quantification process. A narrowing of the peak at 1.5 MeV from Fig. 5.17 (a) to Fig. 5.17 (g) indicates that the overall CuGaS$_2$ layer gets thinner as one measures from the leading edge to the trailing edge. Cross-sectional SEM measurements confirm this decrease in thickness. The surface layer consistently measures Cu-rich with little change in the composition in the direction of carrier gas flow.

![Cross-sectional SEM micrograph of the layer described in Fig. 5.17. The marker indicates 2 µm.](image)

The simulated composition of the underlying layer displayed no such consistency with apparently nearly stoichiometric regions occurring at 1, 3 and 6 mm, Cu-rich regions at 4 and 5 mm, and Ga-rich regions at 2 and 7 mm. Little or no trend in the degree of surface roughness was found as one analysed across the layer surface. The composition values obtained from RBS are averaged over the whole thickness of the film in order to compare with the values obtained by EDS. Both sets of values have been included in Table 5.3. It is quite clear that the Cu- and Ga-content vary significantly depending upon the technique used. However, it is interesting to note that the S-content is almost identical for both techniques.
Table 5.3. Change in composition of thin film across sample surface as measured by both RBS and EDS.

<table>
<thead>
<tr>
<th>Distance [mm]</th>
<th>Average composition from RBS [at.%]</th>
<th>Composition from EDS [at.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Ga</td>
</tr>
<tr>
<td>1</td>
<td>30</td>
<td>19</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>23</td>
</tr>
<tr>
<td>3</td>
<td>29</td>
<td>19</td>
</tr>
<tr>
<td>4</td>
<td>34</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>34</td>
<td>14</td>
</tr>
<tr>
<td>6</td>
<td>28</td>
<td>19</td>
</tr>
<tr>
<td>7</td>
<td>26</td>
<td>22</td>
</tr>
</tbody>
</table>

Quantification results by RBS are theoretically more accurate for the heavier elements, but S (having the lowest atomic mass) is quite clearly the most accurately measured element of the three. This is better understood when one considers the similar masses of Cu and Ga. The nearness in energy of the back-scattered particles off either of these elements creates a significant overlap in the RBS spectra, thereby leading to inaccuracies in any quantification results. Another significant conclusion can be drawn from this comparison. Quantification by RBS repeatedly suggests more Cu in the layer than is suggested by EDS. The layer is analysed as Cu-rich by RBS and Ga-rich by EDS. This result lends credence to the possibility that the method of analysing composition by EDS by utilizing of the Cu-L, Ga-L and S-K X-ray lines possibly contributes to the consistently measured Ga-rich composition of most layers produced in this study.

5.4 Summary

In conclusion, non-uniformities in the composition and surface morphology across the substrate surface were observed both laterally and in the direction of the carrier gas flow. A decrease in the Cu/Ga ratio of the solid in the direction of the carrier gas flow suggested Cu was the minority species at the growth interface. An increase in the VI/(I+III) ratio in the vapour phase led to a drastic reduction in the Cu content of the grown thin films, which suggests that a pre-reaction between the Cu and S metalorganics occurs. It was speculated that S aided the incorporation of Cu into the CuGaS$_2$ lattice,
and as such, an increase in the growth temperature (and hence decrease in the S-content at the growth interface) resulted in an increase in the Cu/Ga ratio of the solid. Ga-rich to near stoichiometric material (in this work determined from EDS for Cu/Ga ratios in the solid less than ~0.82-0.85) exhibited a significantly smoother surface morphology than Cu-rich material.

A Cu-rich sample grown on a Si substrate was analysed by RBS for the purpose of comparing the measured composition with that obtained from the more commonly used method (i.e. EDS). Due to a large peak overlap between the Cu and Ga contributions in the RBS spectra, and the rough surface morphology, considerable inconsistencies were found in the Cu/Ga ratio as determined by each technique. However, the S/(Cu+Ga) ratios determined by each technique were comparable. In order to accurately simulate the RBS spectra, it was necessary to describe the sample in terms of smoother, underlying layer and rougher surface layer.
CHAPTER 6

STRUCTURAL CHARACTERISATION AND PHASE IDENTIFICATION

To comprehensively characterise the structure of a material it is vitally important to make use of a variety of techniques, since no single technique alone is capable of fully describing the epilayers grown. In this study, XRD proved an important tool for identifying the phases present as well as determining the orientation of the material with respect to the substrate used. However, it will be shown in this chapter that there are a number of different structures of CuGaS$_2$ that differ in the arrangement of the metal cations within the crystal lattice. These structures display very similar XRD reflections to that of the desired chalcopyrite crystal structure. In addition, there are a number of other phases with comparable interplanar spacings, creating significant confusion when attempting to interpret the XRD spectra.

6.1 Typical XRD spectra for CuGaS$_2$

In Fig. 6.1 a simulation of the expected 2θ reflections for a powder sample of CuGaS$_2$ is shown, and the lattice parameters of $a = 5.360$ Å and $c = 10.490$ Å as listed in the Powder Diffraction File (PDF 6-0358). The spectrum was generated using JEMS electron diffraction software (Stadelmann, 1999).
Figure 6.1. Simulated XRD spectrum from a powder sample of CuGaS$_2$ using 5.360 Å and 10.49 Å as the $a$ and $c$ lattice parameters respectively.

From this simulated X-ray diffraction spectrum one would expect that for a polycrystalline thin film of CuGaS$_2$, the reflection from the 112 plane would be the most noticeable, in addition to a number of the other more noticeable reflections such as those from the 220, 204 and 312 planes. In this study, however, the main interest lies in the epitaxial growth of CuGaS$_2$ on GaAs(001) substrates. Growth of this nature is possible through the positioning of the CuGaS$_2$ sub-lattice on the GaAs(001) substrate surface in three possible orientations. These orientations are depicted in Fig. 6.2 [Bauknecht, PhD. Dissertation 1999]. The orientation depicted in Fig. 6.2 (a) is termed $c$-axis growth of the chalcopyrite owing to the $c$-axis being orientated normal to the substrate surface. The two orientations depicted in Fig. 6.2 (b) are analogous to one another and are termed $a$-axis growth for similar reasons described above. For the growth of CuGaS$_2$ on GaAs(001), the mismatch between the lattice parameter of the substrate and the $a$-lattice parameter of CuGaS$_2$ is smaller than between that of the substrate and $c/2$. Hence, one would expect $c$-axis growth to be preferred.
Figure 6.2. Crystal orientations possible for the heteroepitaxial growth of the chalcopyrite CuGaS$_2$ on an (001)-orientated substrate with a zincblende crystal structure: $c$-axis growth (a) and $a$-axis growth (b) (Bauknecht, 1999).

However, for the epitaxial growth of thin films on a substrate, one must also consider the thermal expansion mismatch between the epilayer and substrate. The values given in Table 6.1 list the lattice and thermal expansion mismatch for both orientations of epitaxial growth. A smaller lattice mismatch between epilayer and substrate occurs for $c$-axis orientated material than for $a$-axis orientated material. However, the thermal expansion mismatch for this growth orientation is more than twice that for $a$-axis growth.

Table 6.1 Lattice and thermal expansion mismatch coefficients ($\alpha$) for $a$-axis and $c$-axis oriented epitaxial growth on GaAs(001) substrates.

<table>
<thead>
<tr>
<th>Substrate plane</th>
<th>Growth plane</th>
<th>Fitted parameter</th>
<th>Type of growth</th>
<th>Lattice mismatch coefficient (%)</th>
<th>Thermal expansion mismatch coefficient(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs(001)</td>
<td>(001)</td>
<td>$a$</td>
<td>$c$-axis</td>
<td>-4.88</td>
<td>+64.7*</td>
</tr>
<tr>
<td></td>
<td>$c/2$</td>
<td>$a$-axis</td>
<td>-7.28</td>
<td></td>
<td>+30</td>
</tr>
</tbody>
</table>

* Calculated using $\alpha_{\text{c-axis}}$ of CuGaS$_2$ from Bodnar and Orlova, 1983.
The majority of layers analysed by XRD in this study exhibited a combination of polycrystalline and c-axis orientated epitaxial growth. Layers which analysed significantly non-stoichiometric sometimes exhibited additional peaks relating to other phases and other structure types. However, a-axis epitaxial growth was never observed as the dominant orientation for an epilayer. Results in this chapter will show that the lattice mismatch is the overriding mechanism during epitaxial growth of the material in this study. This suggests that the thermal expansion mismatch between the CuGaS$_2$ epilayer and the GaAs(001) substrate plays only a minor role at growth temperatures of between 550 °C and 600 °C.

6.2 Uniformity of XRD measurements across sample surface

It has been shown how the composition of each epilayer varies across the sample surface to a degree which is dependent on a number of different growth conditions. To clearly distinguish between changes in the properties of grown epilayers induced by non-uniformities in the reactor and by changes in the growth parameters, it was vital to perform measurements in comparable areas between individual samples. For this reason, all measurements (i.e. composition, surface morphology, photoluminescence, as well as XRD) were performed on the leading edge of the sample surface. XRD, however, is a technique which examines a relatively large surface area and requires sufficient crystalline material in order to observe peaks intense enough to be measured by the XRD detector. Fig. 6.3 illustrates how a typical sample was positioned on the susceptor. The sample was cleaved for further analysis (e.g. thickness measurements) from the underside of the epilayer opposite to the direction of the carrier gas flow (see arrow, ◄). The highlighted region of interest, which was approximately 1 mm$^2$ in size, was taken as a representative region for the epilayer and all other results (e.g. SEM, EDS, TEM, Raman, etc.) pertain to this region. This was done in order to maintain consistency between consecutive samples.

Fig. 6.4 illustrates the difference in the XRD spectra (between 29 and 36 °2θ) for different regions of a sample grown at 550 °C over a period of 2 hours with a total carrier
gas flow of 4.95 l/min. XRD analysis of the whole sample, the region of interest only, and the trailing edge only of the sample placed within the X-ray beam are given in the bottom, middle and top spectra respectively. The estimated compositions are ~ Cu:24 at.%, Ga:27 at.%, S:49 at.% and ~ Cu:23 at.%, Ga:28 at.%, S:49 at.% for the region of interest and trailing edge sections, respectively.

Figure 6.3. Schematic illustration of the position of the GaAs(001) substrate on the susceptor during growth. The dashed line indicates the line along which the sample was cleaved, and the shaded area highlights the region of interest, which is analysed in greater detail by other techniques.

The lower spectrum in Fig. 6.4 is dominated by the 002 GaAs reflection at 31.56 °2θ. Two other peaks, of relatively the same intensity, are identified at 29.00 and 34.16 °2θ respectively. The positions of these peaks match well with the 29.06 and 34.06 °2θ reported for the unstrained values of the 112 and 004 reflections from a powder sample of CuGaS₂. The value of 34.16 °2θ is larger than the unstrained value owing to the distortion in the unit cell as the epilayer attempts to lattice match with that of the substrate. From this spectrum it would appear that polycrystalline and epitaxial CuGaS₂ is present in approximately the same proportion owing to the similar intensities between the 112 and 004 reflections. However, when the spectra from the region of interest, trailing edge and that of the whole sample are compared, it appears that 004 orientated growth is dominant.
Figure 6.4. XRD spectra of a near stoichiometric CuGaS$_2$ thin film collected from: the whole sample (bottom spectrum), region of interest only (middle spectrum) and the trailing edge only (top spectrum). The growth parameters for this sample are as indicated.

This suggests that epitaxial growth is prevalent in regions closer to the centre of the susceptor, whereas polycrystalline growth dominates for regions closer to the reactor walls (for which a higher Cu/Ga ratio in the solid is usually measured - see Fig. 5.2). These differences in the XRD once again highlight the need for measurements to be performed in a standard region.

6.3 Additional phases

The formation of additional phases as a result of non-ideal growth parameters and composition can severely hamper the epitaxial growth of CuGaS$_2$. XRD results depicting such phases (as well as those phases expected during the growth of other chalcopyrites such as CuInSe$_2$ and CuGaSe$_2$) have been reported by a number of authors (Orsal et al., 2000; Chichibu et al., 1998; Albin et al., 1988; Caballero and Guillen, 2002; Guillén and Herrero, 2002; Reddy and Reddy, 1991, Xu et al., 2004). The normal approach to the identification of these phases would be to study the ternary phase diagram illustrated in
Fig 2.6. Using this phase diagram and previously published results from others authors as a guide, the simulated XRD spectra for each of the most likely phases are graphically illustrated in Fig. 6.5. The $d$ values used for each of the phases were obtained from the powder diffraction files. The positions of some of the more relevant and overlapping reflections for each of the phases illustrated in Fig. 6.5 have been tabulated in Table 6.2.

![Simulated XRD spectra for various phases](image)

**Figure 6.5.** Simulated 2θ peak positions for a variety of phases relevant to the growth of CuGaS$_2$. 
A number of different phases exhibit reflections at very similar 2θ positions to those expected for a powder sample of CuGaS$_2$. Relevant examples of this ambiguity would include the positions of the 102 reflection of CuS (covellite), occurring at 29.20°2θ, and the 112 reflection of CuGaS$_2$. In addition to the covellite phase, a number of other Cu$_x$S$_y$ phases exhibit reflections close to the 2θ value of ~29°, such as the 342 reflection of Cu$_2$S occurring at ~29.26°2θ. The GaS and Ga$_2$S$_3$ phases also exhibit reflections at 29.36 and 29.65°2θ respectively. Normally, combined analysis by EDS and XRD is sufficient to accurately characterise the phase(s) responsible for the observed reflection(s).

**Table 6.2.** Abbreviated list of possible secondary phases expected in addition to the chalcopyrite CuGaS$_2$, and their expected XRD peak positions.

<table>
<thead>
<tr>
<th>Phase</th>
<th>System</th>
<th>Lattice parameters</th>
<th>Relevant reflections</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-CuGaS$_2$</td>
<td>tetragonal</td>
<td>$a = 5.360 \text{ Å}$ $c = 10.49 \text{ Å}$</td>
<td>plane: 112 200 004 220 204 312 316 2θ: 29.06° 33.41° 34.06° 47.99° 48.48° 57.17° 57.27°</td>
</tr>
<tr>
<td>CuS (covellite)</td>
<td>hexagonal</td>
<td>$a = 3.792 \text{ Å}$ $c = 16.34 \text{ Å}$</td>
<td>plane: 102 103 104 2-10 2-12 204 207 2θ: 29.20° 31.68° 34.90° 47.81° 49.15° 60.54° 69.70°</td>
</tr>
<tr>
<td>Cu$_2$S (chalcolite)</td>
<td>orthorhombic</td>
<td>$a = 11.88 \text{ Å}$ $b = 27.32 \text{ Å}$ $c = 13.49 \text{ Å}$</td>
<td>plane: 342 420 191 282 380 2θ: 29.26° 31.03° 31.47° 33.54° 34.74°</td>
</tr>
<tr>
<td>GaS</td>
<td>hexagonal</td>
<td>$a = 3.585 \text{ Å}$ $c = 15.50 \text{ Å}$</td>
<td>plane: 100 101 012 013 006 017 010 2θ: 28.68° 29.36° 31.03° 33.64° 34.83° 45.59° 50.67°</td>
</tr>
<tr>
<td>α-Ga$_2$S$_3$</td>
<td>monoclinic</td>
<td>$a = 11.14 \text{ Å}$ $b = 6.41 \text{ Å}$ $c = 7.038 \text{ Å}$ $β = 121.2°$</td>
<td>plane: -311 -112 310 021 -220 -402 2θ: 27.77° 29.65° 31.44° 31.66° 33.70° 37.78°</td>
</tr>
<tr>
<td>ϕ-CuGa$_2$</td>
<td>tetragonal</td>
<td>$a = 2.836 \text{ Å}$ $c = 5.847 \text{ Å}$</td>
<td>plane: 100 110 112 200 104 2θ: 31.59° 45.28° 55.62° 65.96° 72.87°</td>
</tr>
</tbody>
</table>

It is important to be aware that there are a large number of variations for each phase (i.e. different structural variants/polytypes may occur at different temperatures, phases with different structure types, etc.), and this can significantly complicate the interpretation of XRD spectra. For the Cu$_x$S$_y$ phases alone, a total of 51 possible structures (although many of them comparable) were calculated. In addition to this intricacy, further confusion may arise if a preferred orientation exists for a particular phase. For example, one might expect the 103 line to dominate for polycrystalline CuS. However, a preferential orientation of the (102) plane normal to the substrate surface might create
some confusion since several other phases exhibit similarly positioned reflections \((e.g. 112 \text{ of CuGaS}_2)\).

Of all the grown layers investigated, only one displayed a doublet at an angle \(2\theta \sim 29^\circ\) (the position of the dominant line expected for polycrystalline CuGaS\(_2\)). The XRD spectra for this layer are illustrated in Fig. 6.6. This sample was grown with a high I/III and VI/(I+III) in the vapour phase of 40 and 11 respectively.

**Figure 6.6.** (a) An XRD spectrum of a sample displaying a doublet at \(\sim 29^\circ \theta\) and additional peaks relating to a secondary phase. The \(2\theta\) range between 28 and 31 \(^\circ\) has been magnified in (b).

The three spectra illustrated in Fig. 6.6 (a) were collected from the whole sample (bottom spectrum), the leading edge (region of interest) only (middle spectrum), and the trailing edge (top spectrum). A number of peaks can be seen in the range from 25 to 75 \(^\circ\)\(2\theta\). The doublet at \(\sim 29^\circ \theta\) in each of the spectra is better resolved in Fig 6.6 (b). Two peaks at 29.06 \(^\circ\)\(2\theta\) and 29.36 \(^\circ\)\(2\theta\) have been fitted to this region and have been labeled #1 and #2 respectively. The lower angle reflection (#1) is attributed to the 112 plane of polycrystalline CuGaS\(_2\). A weak shoulder is seen on the low-angle side of the 200 GaAs reflection in the bottom two spectra of Fig. 6.6 (a) only (labeled #3) at \(\sim 31.3^\circ \theta\). Lastly, a broad peak can be seen at \(\sim 60.5^\circ \theta\) in the same two spectra, which has been labeled #4. One cannot assume that the additional peaks (#2, #3, and #4) are attributed to a
Cu$_x$S$_y$ phase owing to the high I/III and VI/(I+III) ratios in the vapour phase. The significantly Ga-rich nature of this sample in the solid (Cu:20.4 at.%, Ga:29.1 at.% S:50.5 at.% for the region of interest) is attributed to the high VI/(I+III) ratio in the vapour phase resulting in a more severe parasitic reaction between the precursors DtBS and Cu(hfac)$_2$-EtN$_3$. A severe compositional gradient existed across the surface of this sample with the Cu/Ga ratio in the solid changing from 0.70 at the leading edge to 0.31 at the trailing edge. The relative intensities of peak #1 to peak #2 ($I_1/I_2$) are illustrated in Fig. 6.6 (b). There is a change in the dominant reflection between leading edge and trailing edge, which is attributed to a change in the dominant solid phase from polycrystalline CuGaS$_2$ to a secondary phase, likely a Ga- and S-rich phase, which gives rise to peak #2. However, peaks #3 and #4 are not observed in the spectrum from the trailing edge. Peak #4 is often observed in samples exhibiting an intense 112 reflection (which in turn occurs most often in specimens exhibiting significantly more Cu - which will be discussed presently). Hence, peak #2 is attributed to a Ga$_x$S$_y$ phase and peak #3 and #4 are attributed to a Cu$_x$S$_y$ phase. Further evidence of the formation of secondary phases will be presented within the following sections wherever necessary.

6.4 The effect of changing growth parameters on the XRD spectra

In this section the influence of a change in the growth conditions (such as growth temperature and precursor concentration) on the degree of epitaxy and formation of secondary phases as deduced from XRD spectra recorded for the samples grown, will be discussed and linked to the compositions in the solid phase.

6.4.1 Growth temperature

Three layers with similar compositions, but grown at different substrate temperatures, were chosen to investigate the effect of temperature on the epilayer quality. The XRD spectra for each of these layers are illustrated in Fig. 6.7. The solid compositions for each of the three epilayers grown at 550 °C, 575 °C and 600 °C were estimated by EDS to be: Cu:23.7 at.%, Ga:27.0 at.%, S:49.3 at.%; ~Cu:24.0 at.%, Ga:27.0 at.%, S:49 at.%;
Cu:24.5 at.%, Ga:26.5 at.%, S:49.0 at.% respectively. As mentioned previously, these values relate to the region of interest only.

Figure 6.7. (a) XRD spectra of three samples with a similar composition grown at 550 °C (bottom), 575 °C (middle) and 600 °C (top). The 2θ range between 28 ° and 36 ° has been magnified in (b). Intensities have been normalized to the 200 GaAs reflection.

The sample grown at 550 °C displayed two reflections labeled #1 and #2 respectively. A higher order reflection of peak #2 can be seen at ~72.3 °2θ. The position of each of these three peaks match well with the expected positions for the 112, 004 and 008 reflections of CuGaS₂. The sample grown at 575 °C exhibits the 112 reflection only. No suggestion of the 004 and 008 reflections is evident. For the sample grown at 600 °C, an intense 112 reflection was observed approximately an order of magnitude more intense than that of the sample grown at 575 °C. No other peak was observed. Therefore, an increase in growth temperature resulted in an increase in the amount of polycrystalline growth in relation to c-axis orientated epitaxial growth. This result is in direct contradiction to previously published results. Oishi et al. (1995) observed that a decrease in the growth rate of CuGaS₂ by vacuum deposition (to less than 0.18 µm/hour) and/or an increase in the substrate temperature promotes the growth of c-axis orientated epitaxial material. Gossla et al. (1995) also reported that an increase in the substrate temperature (for MBE grown CuInS₂) from room temperature to 400 °C resulted in improved crystal quality. In
a more recent publication by Kessler et al. (2003), the crystallinity of sequentially evaporated Cu(In,Ga)Se$_2$ thin films was shown to improve with an increase in substrate temperature. There are two possible explanations for the present result. The first is related to the slight difference in composition between samples. The Cu/Ga ratio in the solid was calculated to be 0.88, 0.89 and 0.92 for the samples grown at 550 °C, 575 ° and 600 ° respectively. Whilst these values are within experimental uncertainty, the slight increase in this ratio may contribute to the enhancement of polycrystalline growth due to the formation of additional Cu$_x$S$_y$ phases. This result will be studied in greater detail later in this chapter. An alternative reason for this anomaly is related to the degradation of the GaAs substrate during growth. It is well known that GaAs substrates readily lose As atoms from the lattice at temperature in excess of 400 °C. It may be speculated that, owing to the extremely low growth rate of the chalcopyrites by MOVPE, a significant percentage of the substrate surface remains unprotected during the initial stages of growth. During this time, the substrate surface deteriorates and polycrystalline growth occurs. This hypothesis will be proven later in this chapter (section 6.6.2) when high-resolution TEM results of the interfacial region are presented.

6.4.2 Precursor concentration

Fig. 6.8 illustrates the difference in the XRD spectra of two layers grown at 550 °C using the same I/III and VI/(I+III) ratios in the vapour phase. For the second layer (black line) the concentrations of the precursors were decreased by halving their flow rates yet maintaining a total H$_2$ flow of 4.95 l/min. To compensate for the decrease in growth rate for the latter sample, the growth time was doubled to 2 hours. The resulting Cu/Ga and S/(Cu+Ga) ratios in the solid phase were calculated to be 0.83 and 1.13 respectively for the former sample and 0.90 and 0.96 respectively for the latter sample. The XRD spectrum for the sample grown under normal growth conditions, before the concentrations of the precursors were halved (grey line) exhibits reflections from the 004 and 008 planes of c-axis orientated epitaxial CuGaS$_2$ situated at 34.19 and 72.10 °2θ respectively (labeled #1 and #2 respectively). A closer look at the low angle peaks illustrated in Fig. 6.8(b) reveals an additional peak (#4) situated at ~31.9 °2θ, which is
attributed to a S-rich secondary phase of unknown origin. The XRD spectrum of the sample grown with all reagent concentrations halved exhibited a single peak (#3) at 28.99 °2θ, which we attribute to the 112 plane of polycrystalline CuGaS₂. Closer inspection of this spectrum suggests the presence of the same reflection seen in Fig. 6.6 at ~31.3 °θ. The enhancement of polycrystalline growth with a decrease in growth rate is also in direct contradiction to the reported results of Oishi et al. (1995) for the growth of CuGaS₂/Si(100).

![XRD spectra diagram](image)

**Figure 6.8.** (a) XRD spectra of two samples grown at 550 °C with identical I/III and VI/(I+III) ratios in the vapour phase. The spectrum represented in grey is for a layer grown with the higher precursor concentrations for 1 hour, whereas the spectrum represented in black is for a sample grown for 2 hours using half the concentration of the precursors. The 2θ range between 28 and 36 ° has been magnified in (b). Intensities have been normalized to the 200 GaAs reflection.

In section 6.4.1 it was suggested that an increase in growth temperature leads to an increase in the degradation of the substrate and hence a corresponding decrease in the degree of epitaxy in the thin film. A decrease in the growth rate, such as when the reagent concentrations are halved, would lead to a similar result since a larger percentage of the GaAs substrate remains exposed (and susceptible to the desorption of As atoms) for a longer time at the start of the growth period. This would explain the loss of an epitaxial relationship with the substrate when the concentration of precursors is decreased.
6.4.3 Cu/Ga ratio in the solid

EDS analysis of all samples grown in this study indicated that most epilayers were Ga-rich in composition. In chapter 5 it was mentioned that the EDS measurement procedure possibly overestimates the Ga-content of the grown thin films. It was speculated that the transition from Ga-rich material to Cu-rich material occurred at a measured value of ~23 at.% Cu in the solid (Cu/Ga ratio in the solid ≈ 0.85).

![Figure 6.9](image)

Figure 6.9. XRD spectra of a number of samples representing a wide range of Cu/Ga ratios in the solid. All samples were grown on GaAs(001) substrates at 550 °C for a period of 2 hours. The total carrier gas flow was maintained at 4.95 l/min. Spectra have been normalized according to the intensity of the 004 GaAs reflection. Spectra have been arranged from bottom to top in order of increasing Cu/Ga ratio in the solid and labeled A to H accordingly.

Fig. 6.9 depicts the XRD spectra from a series of thin films with a solid composition covering a wide range of Cu/Ga ratios in the solid. All samples were grown with a total carrier gas flow of 4.95 l/min, for a period of 2 hours at a growth temperature of 550 °C. The lower spectrum (labeled A) exhibits two peaks at ~34.3 °2θ and ~72.6 °2θ respectively, which closely coincide with the expected positions of the 004 and 008
reflections of CuGaS$_2$. The presence of these two reflections alone seems to suggest epitaxial growth. However, clearly the composition of this layer is far from stoichiometric (Cu: 10 at.%, Ga: 33 at.%, S: 57 at.%). In fact the ratios of these elements (Cu:Ga:S = 1:3:5) suggest that the ordered-defect compound (ODC) CuGa$_3$S$_5$ constitutes the bulk of the sample. In increasingly Ga-rich samples the density of V$_{Cu}$ increases: the unit cell shrinks in both the $a$ and $c$ directions and approaches that of a cubic unit cell. There is a corresponding increase in the angle of diffraction of incident X-rays according to Bragg’s equation. This shift in the observed reflections has been reported by a number of authors such as Xu et al. (2004) for the Cu-In-Se system and Orsal et al. (2000) for MOCVD grown CuGaSe$_2$. This shift to higher 2$\theta$ values for decreasing Cu/Ga ratio in the solid is not restricted to the 004 and 008 reflections. An increase in the cubic nature of the unit cell and loss of tetragonal distortion leads to a shift in the 2$\theta$ positions of all peaks according to the equation (Albin et al., 1988):

\[
\Delta 2\theta = 2 \left( \sin^{-1} \left( \frac{\lambda^2}{4a^2} \right) \left[ h^2 + k^2 + \left( \frac{l}{\delta} \right)^2 \right] \right)^{1/2} - \sin^{-1} \left( \frac{\lambda^2}{4a^2} \left[ h^2 + k^2 + \left( \frac{l}{2} \right)^2 \right] \right)^{1/2} \tag{6.1}
\]

where $h$, $k$ and $l$ are the tetragonal parameters, and $\delta = c/a$ is the tetragonal distortion.

The spectrum labeled B in Fig. 6.9 is from a sample with a higher Cu-content (Cu: 16 at.%, Ga: 31 at.%, S: 53 at.%). This spectrum exhibits the same reflections as that of the previous sample, but the shift to higher 2$\theta$ values is not as severe. Spectrum C is for a layer with a Cu/Ga ratio in the solid of 0.84. Although this spectrum exhibits the same set of reflections as the first two, it should be compared with spectrum D, which is from a layer with an identical Cu/Ga ratio in the solid. The spectrum of this layer is entirely different, with only one peak being observed at a position consistent with the expected position of the 112 peak of CuGaS$_2$. This irregularity can be attributed to the sensitivity of the growth mechanism, hence the orientation, of grown epilayers for compositions near the ideal stoichiometric composition (which is suspected to occur for a measured
Cu/Ga ratio of ~0.85). The spectra labeled E to H in Fig. 6.9 all exhibit a dominant 112 reflection, suggesting polycrystalline growth occurs readily in Cu-rich material.

It must be mentioned that the presence of only a 112 reflection for a grown thin film might at first glance suggest epitaxial growth of 112 orientated CuGaS$_2$. However, attention must be drawn to the orientation of the GaAs(001) substrate. A hexagonal arrangement of atoms occurs in the (112) plane of the CuGaS$_2$ lattice and thus the epitaxial relationship CuGaS$_2$(112)/GaAs(001) is highly unlikely. A preferential orientation of the domains and crystallites in the [112] direction, however, is perfectly plausible. This can be explained in terms of the closest-packed planes of a particular crystal structure. The {112} planes have the densest packing and hence present the lowest energy configuration for a nucleus (ignoring any interaction from the GaAs substrate). Hence, the 112 peak for a polycrystalline thin film will appear significantly more intense than that which would usually be expected for a true polycrystalline powder sample of CuGaS$_2$.

The behaviour of each peak can also be described in terms of the composition of a sample. The XRD spectra of a number of samples exhibiting the 004 reflection at ~34.2 °2θ are illustrated in Fig. 6.10. These samples represent a wide range of compositions with a Cu/Ga ratio of between 0.32 (bottom spectrum) and 1.29 (top spectrum). The position of this peak is plotted as a function of the Cu/Ga ratio in the solid in Fig. 6.10 (b). From this graph it can be seen that little or no shift is observed in the peak position for a change in the Cu/Ga ratio from 1.29 to 0.81. However, a further decrease in the Cu/Ga ratio to 0.50, and more significantly to 0.32, results in a substantial shift to higher 2θ values and a distinct broadening of the peak. The shift to higher angles can be attributed to two processes: c-axis orientated epitaxial growth results in a shortening of the c-axis as the base plane undergoes tensile strain in an attempt to match the lattice parameter of the GaAs(001) substrate. This shortening of the c-axis will lead to a shift in the 004 peak position to higher angles. However, this shift is exaggerated for significantly Ga-rich material owing to the formation of the ODC, such as CuGa$_3$S$_5$. This phase has a smaller lattice parameter than that of the chalcopyrite, and as such the lattice-
mismatch with the substrate increases. The broadening that is observed can also be ascribed to an overlap of the 004 and 002 peaks for both CuGaS$_2$ and CuGa$_3$S$_5$ respectively. It is clear that a shift in this peak only occurs when the composition becomes increasingly Ga-rich and no shift to lower 2θ values occurs in the peak position for samples which are increasingly Cu-rich. It is well-known that growth under increasingly Cu-rich and S-rich conditions promotes the formation of CuGaS$_2$ in addition to Cu$_x$S$_y$ binary phases (Scheer et al., 1993; Gossla et al., 1995; Alvarez-García et al., 2000). Growth under increasingly Ga-rich and S-rich conditions might promote the formation of the ordered defect compounds such as CuGa$_3$S$_5$, CuGa$_4$S$_7$ and CuGa$_5$S$_8$; however no such evidence for the formation of these ODC phases in the Cu-Ga-S system has been reported to date. Although the formation of Ga$_x$S$_y$ binaries are possible, they do not form as easily as the Cu$_x$S$_y$ binary phases (Metzner et al., 1991; Walter et al., 1992).

The tendency for the 004 peak position to stabilize at a Cu/Ga ratio in the solid of ~0.81 is further proof that the actual transition from Ga-rich material to Cu-rich material occurs for material which is measured to be distinctly Ga-rich (i.e. Cu/Ga ratio ≈ 0.85).

The average grain size of the material can be estimated using Scherrer’s formula.

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

6.2

where $\lambda$ is the wavelength of the X-rays (Cu-K$_\alpha$ radiation = 0.15405 nm), $\beta$ is the full-width at half-maximum (FWHM) in radians and corrected for the instrumental broadening (~6.1x10$^{-4}$ radians), and $\theta$ is given in degrees. The estimated grain size distribution of the material generally decreases with increasing Cu/Ga ratio in the solid. This would indicate an increase in crystal quality with an increase in the Cu/Ga ratio, which is in agreement with previously published work for the chalcopyrites CuInS$_2$ and CuGaSe$_2$ (Hunger et al., 2000; Chichibu et al., 1998; Orsal et al., 2000). The range of grain sizes found in this work (~40-110 nm) is significantly smaller than the value of ≤1.3 µm reported by Hunger et al. (2000) for the growth of CuInS$_2$/Si(111) by thermal evaporation. However, Cieslak et al. (2003) reported a grain size of 55 nm for MBE-
grown CuGaS₂/Si(111). In that study, the grain size was found to be far less than the layer thickness indicating a high density of stress and stacking faults within the material.

**Figure 6.10.** (a) XRD spectra highlighting the 004 peak for a number of samples covering a wide range of compositions. The Cu/Ga and S/(Cu+Ga) ratios in the solid are indicated alongside each spectrum. (b) Peak position (solid squares) and estimated grain size using Scherrer’s formula (open squares) as a function of the Cu/Ga ratio in the solid.

The XRD spectra of a number of samples exhibiting the 112 reflection at ~29°2θ are illustrated in Fig. 6.11 (a). These samples represent a range of compositions with a Cu/Ga ratio of between 0.70 (bottom spectrum) and 0.91 (top spectrum). The peak positions are plotted as a function of the Cu/Ga ratio in the solid in Fig. 6.11 (b). It would appear that there is no significant shift in the position of this peak with changing Cu/Ga ratio in the solid. This may be attributed to the absence of any ODC. The axes in Fig 6.10 (b) and Fig. 6.11 (b) cover the same range, and it is immediately noticeable that the Cu/Ga ratio range for which the 112 reflection was observed (0.91 to 0.70) is significantly smaller than the range for which the 004 reflection was observed (1.29 to 0.32). One cannot be sure if the 112 reflection will indeed undergo a shift for very Ga-rich material as described by Albin et al. (1988). The additional peak situated at
29.40°2θ is attributed to a Ga$_x$S$_y$ phase, which could not be positively identified by XRD. The approximate grain sizes (see Fig. 6.11 (b)) for those samples with XRD spectra illustrated in Fig. 6.11 (a) follow no observable trend and cover a range of values similar to those in Fig. 6.10 (b).

![Graph](image)

**Figure 6.11.** (a) XRD spectra highlighting the 112 peak for a number of samples covering a range of compositions. The Cu/Ga and S/(Cu+Ga) ratios in the solid are indicated alongside each spectrum. (b) Peak position (solid squares) and estimated grain size using Scherrer’s formula (open squares) as a function of the Cu/Ga ratio in the solid.

### 6.5 Sulphur-termination of the GaAs substrate prior to growth

The growth rate for CuGaS$_2$/GaAs(001) by atmospheric pressure MOCVD is ~0.1 µm/hour. Assuming an approximate c-parameter of 10.5 Å and c-axis orientated epitaxial growth, this value translates to ~1.5 monolayers of material per minute. For a growth run where the standard initial growth procedure was employed (see section 4.1.3), the AsH$_3$ (which flowed through the reactor during the annealing step and subsequent cool down to growth temperature in order to prevent substrate decomposition) was switched out of the reactor at approximately the same time that the Cu, Ga and S
precursors were introduced into the reactor. There is therefore a minimum period of almost a minute during which arsenic atoms may desorb. This may cause severe damage to the substrate surface and inhibit/prevent epitaxy. To counter this problem, and without maintaining an AsH$_3$ overpressure during the growth stage, the DtBS was introduced into the reactor tube whilst the AsH$_3$ was flowing. The AsH$_3$ was then decreased slowly before being switched to the vent line. Any dangling bonds resulting from desorbed As atoms may then be terminated by the S atom.

![Figure 6.12](image)

**Figure 6.12.** XRD spectra for three samples grown on GaAs(001) substrates, which were submitted to different pre-treatments. The spectrum positioned at the bottom represents a sample having undergone no S-termination prior to growth, whereas the spectra in the middle and top represents samples submitted to 1 and 5 minutes of S-termination respectively. The I/III and VI/(I+III) ratios in the vapour phase were 37 and 9 respectively.

The S-passivation of GaAs growth surfaces (for the purpose of increasing the current gain of the GaAs/AlGaAs heterostructure bipolar transistors) was first attempted in the late-eighties by Sandroff *et al.* (1987) by using Na$_2$S⋅9H$_2$O. More recently Si(111) and Si(001) substrates were S-terminated prior to the growth of CuInS$_2$ and CuGaS$_2$ by MBE (Metzner and Hahn, 2001; Metzner *et al.*, 2002). Tiwari *et al.* (2000) has also used this technique for the growth of CuIn$_x$Se$_{y}$ on Si(111) substrates by MBE. This group
speculated that the group VI species, namely Se$_8$ molecules were cracked at the hot surface to yield S$_4$, Se$_2$ and Se, which then terminated the Si dangling bonds.

Fig. 6.12 represents the XRD spectra of three layers grown with different growth initialisation procedures. The bottom spectrum represents a sample grown under standard conditions, whereby the AsH$_3$ was switched out of the reactor at approximately the same time that the Cu(hfac)$_2$·Et$_3$N, TEGa and DtBS were introduced. The middle spectrum represents a sample grown after 1 minute of S-termination. The DtBS was introduced 1 minute prior to the Cu(hfac)$_2$·Et$_3$N and TEGa entering the reactor. During this minute, the AsH$_3$ was ramped down at a constant rate from 100 sccm to 0 sccm. The top spectrum represents a sample grown after a 5 minute S-termination. For this sample, the DtBS was introduced 5 minutes prior to the introduction of Cu(hfac)$_2$·Et$_3$N and TEGa, during which time, the AsH$_3$ was also ramped down at a constant rate from 100 sccm to 0 sccm. The Cu/Ga and S/(Cu+Ga) ratios in the solid are indicated in Fig. 6.12 (b). The sample grown by the standard process exhibited polycrystalline growth only (deduced from the dominant 112 peak), while the layers grown after S-termination of the GaAs surface appear to have grown epitaxially (as deduced from the dominance of the 004 and 008 peaks). The FWHM of the 004 peaks were 0.27 °2θ and 0.26 °2θ for the layers grown after 1 minute and 5 minutes of S-termination, respectively.

6.6 Structure types and TEM

In section 2.5 the various crystal structures of CuGaS$_2$, which differ only in the position of the metal atoms within the crystal lattice, were discussed. A powder diffractometer such as the one used in this study cannot conclusively differentiate between each of these structure types. This section illustrates how this ambiguity is addressed through the use of TEM diffraction patterns, which (under particular conditions) enable one to identify the crystal structure present in the grown material.

6.6.1 Conventional TEM
The possible formation of CuAu-, CuPt- and disordered zincblende-type material in addition to the chalcopyrite phase has been discussed in section 2.5. To conclusively determine which of the possible structure types are responsible for the observed XRD lines, JEMS electron diffraction software (Stadelmann, 1999) was used to simulate transmission electron diffraction patterns along different zone axes for each of the above possible structures. The cubic <211> zone-axes allow one to differentiate between all of the above types of ordering since different patterns exist for each structure type. These electron diffraction patterns are depicted in Fig. 6.13. The electron diffraction pattern in Fig. 6.13 (a) is that of the equivalent <212> orientation for c-axis grown chalcopyrite material. The electron diffraction pattern of the <211> orientation of zincblende material is depicted in Fig. 6.13 (b) (solid circles). The <211> orientation (equivalent cubic indices) of the CuAu-type material exhibits a similar electron diffraction pattern to the zincblende material. An extra set of spots (open triangles), however, is introduced. Similarly, CuPt-type ordering introduces a different set of extra spots (open circles).

![Figure 6.13](image)

**Figure 6.13.** (a) Simulated electron diffraction pattern for the <212> zone-axis of the chalcopyrite structure and (b) for the <211> zone-axis of zincblende material. Additional spots are shown in (b) for CuAu-type ordering (Δ) and CuPt-type ordering (○).

The electron diffraction pattern in Fig. 6.14 (a) typifies the pattern observed across the underlying layer of a sample grown at 550 °C using the MO sources: Cu(hfac)$_2$-Et$_3$N, TMGa and DtBS, and a I/III and VI/(I+III) ratio in the vapour phase of 14 and 12 respectively. This diffraction pattern matches the simulated electron diffraction pattern for the <211> zone-axis in zincblende material. Although this pattern is identical in orientation to that observed for the GaAs substrate (hence proving epitaxy), it shows that
the epilayer does not have the expected chalcopyrite structure. Very small, embedded regions in the underlying layers, displayed an extra set of spots, indicative of CuPt-type ordering, as shown in Fig. 6.14 (b). Although the formation energy for material with this type of structure is expected to be large (Su and Wei, 1999), one might speculate that because the CuPt-type ordering can accommodate a greater deviation from stoichiometry than the other types of ordering, it is likely that it can occur in non-stoichiometric regions of the epilayer. The equivalent cubic <211> zone-axes could not be obtained when analysing the surface crystallites due to the random orientation that they acquire with respect to the underlying layer and substrate.

![Figure 6.14](image)

**Figure 6.14.** (a) A typical <211> zone-axis electron diffraction pattern of the underlying layers. (b) Small regions within the underlying layers show an extra set of spots indicated by arrows.

Two cross-sectional TEM bright-field images of this epilayer (corresponding to the region depicted in Fig. 6.14) are shown in Fig. 6.15. This sample is the same sample analysed by RBS and described in Fig. 5.17. In the RBS study, a two-layer model was required to describe the sample: a rough, ~0.2 µm thick surface layer, predominantly Cu-rich, which incompletely covered an underlying ~0.33 µm thick layer, which analysed roughly stoichiometric. This value for the underlying layer thickness is a close match to the ~0.22 µm thick as measured here by TEM.

The XRD spectrum for this layer (not shown here - see Branch *et al.*, 2004) exhibited a number of lines attributed to the 112, 200, 004, 220 and 204 reflections of the chalcopyrite material. However, since the TEM suggested that material with a disordered zincblende structure constituted the bulk of this epilayer, the most intense lines of the
XRD spectra (the 004 and 008 reflections) are therefore ascribed to diffraction from the (002) and (004) planes in disordered zincblende material. The lattice parameter of the disordered zincblende underlying layer was calculated from the electron diffraction pattern to be of the order of 5.28 Å. This value is a close match to the value of 5.24 Å as calculated from the positions of the 002 and 004 XRD lines.

Figure 6.15. Cross-sectional TEM micrographs depicting the underlying layer and (a) a faceted crystallite and (b) a rounded crystallite. The marker indicates 0.5 µm. \( \mathbf{B} = [110] \).

Although no conclusive proof for the presence of the chalcopyrite material was found by TEM in the underlying layers, the characteristic splitting of the 220 and 204 lines in the XRD spectrum suggests that the layers do contain chalcopyrite material. This structure type is most likely present within the surface crystallites (as these could not be structurally analysed by electron diffraction). The \( a \) and \( c \) parameters for this material obtained from the 220 and 204 lines were 5.36 Å and 10.53 Å respectively. The value \( c/a = 1.96 \) is in excellent agreement with previously published work on bulk material (Shay and Wernick, 1975).

In conclusion, the use of electron diffraction patterns positively identified the bulk of this epilayer to consist of the disordered zincblende structure type, interspersed with small regions exhibiting CuPt-type ordering. These regions would not have been identified by XRD analysis alone, hence highlighting the value of TEM. Although the presence of the chalcopyrite structure type is evident from the XRD analysis, owing to the splitting of the 220 and 204 lines, TEM analysis could not confirm this.
6.6.2 High resolution transmission electron microscopy (HRTEM)

Fig. 6.16 shows a cross-sectional HRTEM micrograph of a sample of CuGaS$_2$/GaAs(001) grown for a period of 1 hour at a substrate temperature of 550 °C. Cu/Ga and S/(Cu+Ga) ratios of 0.82 and 1.06 respectively were measured by EDS prior to sample preparation. The total carrier gas flow was maintained at 4.95 l/min and the substrate underwent no S-termination prior to the growth process commencing. Unless stated otherwise, a $<110>$ zone axis was used for all TEM imaging and analysis.

![Figure 6.16](image)

**Figure 6.16.** TEM cross section of CuGaS$_2$/GaAs(001) samples in the $<110>$ zone-axis. Films were grown for a period of 1 hour without prior treatment of the substrate by S-termination.

The formation of pyramidal surface crystallites seen in Fig. 6.16 is typical of many of the epilayers grown in this study. Three dimensional growth of thin films by MOCVD is often characterised by a uniform distribution of surface features of approximately the same size. However, crystallites of as little as 10 nm and as large as 200 nm in diameter were found to grow concomitantly over the substrate in this sample. A particularly significant result is the substrate degradation, which was observed for areas of the substrate not protected by the formation of these 3D islands during the growth process. The dashed line in Fig. 6.16 indicates the position of the substrate surface before growth.
The possibility of substrate degradation has been discussed previously in section 6.4. It was shown in that section that the S-termination of the GaAs substrate prior to growth of CuGaS$_2$ significantly enhanced epitaxy.

![TEM cross-section of CuGaS$_2$/GaAs(001) samples in the <110> zone axis. Films were grown for a period of 1 hour without prior treatment of the substrate by S-termination. The substrate is shown on the bottom left, and the dashed line indicates the CuGaS$_2$/substrate interface. Nucleation sites and amorphous regions are labeled NS and Am respectively. A possible area of back-growth (dotted arrow) and twins (arrows) on the {112} planes are also indicated. A lower magnification image showing the entire crystallite is included in the inset.](image)

**Figure 6.17.** TEM cross-section of CuGaS$_2$/GaAs(001) samples in the <110> zone axis. Films were grown for a period of 1 hour without prior treatment of the substrate by S-termination. The substrate is shown on the bottom left, and the dashed line indicates the CuGaS$_2$/substrate interface. Nucleation sites and amorphous regions are labeled NS and Am respectively. A possible area of back-growth (dotted arrow) and twins (arrows) on the {112} planes are also indicated. A lower magnification image showing the entire crystallite is included in the inset.

Fig. 6.17 illustrates the interfacial region of a large crystallite (~200 nm across) approximately an order of magnitude larger than the one labeled A in Fig. 6.16. The inset illustrates the entire crystallite. The large size distribution of crystallites for this particular layer can be better understood in terms of the coalescing of smaller crystallites.
The points at which smaller crystallites first formed have been labeled nucleation sites (NS). Areas of the substrate either side of these sites were exposed for longer periods of time before overgrowth occurred, and experienced significant substrate degradation (original substrate surface marked by the dashed line). Growth occurred outward in a radial direction; however, as a result of the substrate degradation, further enlargement of these crystallites results in a “mushroom-like” appearance. In the middle of Fig. 6.17, highly ordered material occurs immediately above an amorphous region (Am). Since it is unlikely that single-crystalline material (exhibiting the same orientation as the substrate) can grow from an amorphous region, back-growth from nucleation sites toward the substrate is suspected (illustrated by the dotted arrow).

A number of twins in the \{112\} planes are indicated by the solid arrows and seem to originate from regions close to the substrate/epilayer interface. Regions analysed in greater detail are labeled A and B for further discussion. A fast Fourier transform (FFT) image generated from region A clearly shows a double set of spots of identical orientation (confirming epitaxy). The second highlighted region (region B) is shown in Fig. 6.18. In this figure, the micro-twins (mt) are clearly visible extending along the \langle112\rangle directions (white arrows). Evidence of these micro-twins can be seen as an extra set of spots (labeled T) in the FFT image generated from this area (see Fig. 6.18 (b)). Noise can be removed from the original image by applying convenient masks to the FFT image and performing an inverse FFT. An additional effect of this function is the highlighting of specific areas responsible for particular spots in the FFT image. Fig. 6.18 (c) was generated by applying a mask to the primary set of spots indexed in Fig. 6.18 (b), whilst Fig. 6.18 (d) was generated by applying a mask to the twin spots only. Noise is clearly removed from dissimilar regions in each of the filtered images. The region bordered by the dotted line is therefore identified as the twinned region in the crystal.
Figure 6.18. (a) HRTEM cross-sectional image of region B is highlighted in Fig. 6.17. (b) Electron diffraction pattern along a <110> zone axis. Twin spots (T) are indicative of twinning about the <112> twin axis. Microtwins (mt) on the <112> planes are indicated by an arrow and amorphous regions labeled (Am). Inverse FFT image after a mask has been applied (see insets) to indexed spots (c) and twin spots (d).

6.7 Raman spectroscopy

We have shown that Cu is likely the limiting species at the growth interface. Consequently, XRD analysis of Ga-rich layers is largely ineffectual as these films are far thinner than their Cu-rich counterparts. In addition, the macroscopic nature of the XRD technique (the area analysed is approximately 1 cm$^2$) does not allow one to detect smaller inhomogeneities on the sample surface. EDS spectroscopy, whilst useful in measuring
composition, cannot identify the phases present in the film. A technique more suited to the measuring of very thin layers is Raman spectroscopy.

A series of measurements were performed on two samples of CuGaS\textsubscript{2} grown at 550 °C on GaAs(001) substrates, which were of slightly different stoichiometry. The first, described as sample A and illustrated in Fig. 6.19 (a), analysed near stoichiometric Ga-rich with a composition of Cu: 23 at.%, Ga: 27 at.%, S: 50 at.% in the region 1-2 mm from the leading edge of the substrate. It was grown over a period of 2 hours under a I/III and VI/(I+III) ratio in the vapour phase of 37 of 10 respectively. The total carrier gas flow was 4.95 l/min. Three measurements were performed approximately 1 mm apart using a line of 514.5 nm (Argon ion laser) and a 20x objective lens, which provided a spot size of ~1.5 µm in diameter.

The second layer analysed (i.e. sample B) was significantly more Ga-rich, with a composition of Cu: 20 at.%, Ga: 29 at.%, S: 51 at.%. It was also grown over a period of
2 hours, but with a I/III and VI/(I+III) ratio in the vapour phase of 40 and 11 respectively. The total carrier gas flow was also 4.95 l/min. The Raman spectra from various positions along this sample are illustrated in Fig. 6.19 (b). Both sample A and B display the same series of lines, labeled 1-11 in both figures. A substrate-related line is observed at 290 cm\(^{-1}\) corresponding to the GaAs LO mode. It has been mentioned previously that there is a distinct change in the composition of the layer as measurements are performed in the direction of the carrier gas flow. Raman peak positions for both samples A and B have been plotted together as a function of Cu/Ga ratio in the solid (see Fig. 6.20). The frequencies of each mode, when measurements are made ~1 mm from the leading edge, have been listed in Table 6.3, in addition to the maximum deviation of these modes (\(\Delta\omega_0\)) for a change in the Cu/Ga ratio of ~0.23. A comparison has been made with three other studies for completeness. Many other studies have been performed (see section 2.6.4) but these have not been included in Table 6.3 for the sake of brevity.

![Figure 6.20](image-url)  
**Figure 6.20.** Peak positions of Raman modes for both samples A (grey) and B (black) as a function of estimated Cu/Ga in the solid.
Table 6.3. Position and assignment of Raman lines in samples A and B in comparison with lines reported by Refs. 1, 2 and 3.

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<th>( \omega_0^B ) (cm(^{-1}))</th>
<th>( \Delta \omega_0 ) (cm(^{-1}))</th>
<th>( \omega_0 ) (cm(^{-1}))</th>
<th>Assign. (Ref. 1)</th>
<th>( \omega_0 ) (cm(^{-1}))</th>
<th>Assign. (Ref. 2)</th>
<th>( \omega_0 ) (cm(^{-1}))</th>
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The dominant line originating from both films, labeled #7, has been assigned to the \( \Gamma_1 \) mode, known as the breathing mode. This mode is purely ionic in nature and corresponds to the vibration of the group VI atom, in this case sulphur, whilst all other atoms are stationary. This mode is known to be the dominant mode for all chalcopyrites. In this
work it is measured at ~311 cm\(^{-1}\), which is in excellent agreement with previously published results (Gonzalez and Rincon, 1990; Choi and Yu, 1996; Carlone et al., 1980; Bettini and Holzapfel, 1975; Van der Ziel et al., 1974; Koschel and Bettini, 1975; Bodnar et al., 1990). The strong doublet observed at ~387 and ~396 cm\(^{-1}\) (lines #10 and #11) coincides well with the reported energies of the longitudinal \(\Gamma_5\) and \(\Gamma_4\) modes respectively. The higher energy \(\Gamma_4\) and \(\Gamma_5\) modes supposedly originate from the Ga-S bond (Julien and Barnier, 2001). A systematic study of the compositional dependence of the phonon frequencies of different vibrational modes in the Cu-In-Se system was performed by Xu et al. (2004). This group reported a decrease in the energy of the higher frequency \(\Gamma_4\) and \(\Gamma_5\) modes with decreasing Cu/Ga ratio. Although relatively little change is observed in the energies of the lower frequency modes in the present work, a definite shift to higher frequencies is observed for lines #10 and #11, with a decreasing Cu/Ga ratio, in contradiction to observations made by Xu et al. (2004).

The lowest-energy line labeled #1, assigned to the \(\Gamma_5\) mode, is attributed to the Cu-S bond (Julien and Barnier, 2001). From the work of Xu et al. (2004), one would expect an increase in the energy of this mode with a decrease in the Cu/Ga ratio. Although a small shift of ~0.9 cm\(^{-1}\) is observed, it is probably within experimental error. The line labeled #2 at ~95 cm\(^{-1}\) is of unknown origin, but has been assigned to both the \(\Gamma_4\) mode by González et al. (1996) and Julien & Barnier (2001) and the \(\Gamma_5\) mode by Van der Ziel et al. (1974). The line occurring at a frequency of ~115 cm\(^{-1}\) has been attributed to the Cu-Ga bond (Julien and Barnier, 2001) and assigned the \(\Gamma_5\) mode by González et al. (1996) and the \(\Gamma_3\) mode by Carlone et al. (1980). The same study by Julien & Barnier (2001) describes the lines labeled #4, #5, #8 and #9 as originating from the Cu-S-Ga bond complex. No noticeable trend is observed in the relative shift of these lines as a function of the Cu/Ga ratio. Line #6, the higher-energy line of the relatively strong doublet at ~275 cm\(^{-1}\), has been assigned to the longitudinal \(\Gamma_4\) mode by several other groups (González et al., 1996; Van der Ziel et al., 1974).

In order to obtain an indication of the uniformity of phases present on the sample surfaces, a series of spectra were collected over a predetermined area. By measuring the
relative intensity of a Raman line inherent to the thin film in relation to the GaAs LO line at 290 cm\(^{-1}\), one can represent the spatial distribution of a particular phase in the form of an intensity map.

![Unpolarised Raman intensity map for sample A comparing the relative intensity of the 311 cm\(^{-1}\) line with that of the GaAs LO mode (a), and the combined intensity of the lines at 386 cm\(^{-1}\) and 394 cm\(^{-1}\) with that of the GaAs LO mode (b). Lighter and darker regions represent areas of maximum and minimum intensity respectively.](image)

**Figure 6.21.** Unpolarised Raman intensity map for sample A comparing the relative intensity of the 311 cm\(^{-1}\) line with that of the GaAs LO mode (a), and the combined intensity of the lines at 386 cm\(^{-1}\) and 394 cm\(^{-1}\) with that of the GaAs LO mode (b). Lighter and darker regions represent areas of maximum and minimum intensity respectively.

A total of 81 measurements were performed across a 9x9 grid on sample A. The total area measured was ~800x800 μm. The total integrated intensity of the breathing mode, \(\Gamma_1\), relative to that of the GaAs LO mode is represented in Fig. 6.21 (a). An additional mapping was performed comparing the combined intensities of the strong pair of lines occurring at 386 and 394 cm\(^{-1}\) with that of the GaAs line, and is represented in Fig. 6.21 (b). Both maps appear almost identical in contrast, which suggests that the lines used for the mapping functions, that of the dominant line occurring at 311 cm\(^{-1}\) and the pair of lines occurring at 386 and 394 cm\(^{-1}\), originate from the same phase. As we have already assigned each of these lines to the CuGaS\(_2\) phase in Table 6.3, these maps further support our previous assignments. Fig. 6.21 also demonstrates that the CuGaS\(_2\) phase is present in the thin film in the form of crystallites on the substrate surface.
A similar set of measurements were performed on sample B. The *relative* intensity of the \( \Gamma_1 \) mode to the GaAs mode is represented as an intensity map in Fig. 6.22 (a) and the *relative* intensity of the strong doublet at 387 and 397 cm\(^{-1}\) to that of the GaAs mode yields the intensity map illustrated in Fig. 6.22 (b). Regions of maximum intensity are represented by yellow, whereas regions of minimum intensity are represented by navy blue.

![Intensity maps](image)

**Figure 6.22.** Unpolarised Raman intensity map for sample B comparing relative intensity of the 311 cm\(^{-1}\) line with that of the GaAs LO mode (a) and the combined intensity of the lines at 387 cm\(^{-1}\) and 397 cm\(^{-1}\) with that of the GaAs LO mode (b). Regions of maximum intensity are represented by yellow, whereas regions of minimum intensity are represented by navy blue.

The near-identical nature of these maps, once again, illustrate the fact that both the 311 cm\(^{-1}\) and the doublet at 387 cm\(^{-1}\) and 397 cm\(^{-1}\) originate from the same phase (i.e. that of CuGaS\(_2\)). The spatial distribution of this phase is also clearly represented by the contrast in colours. The larger contrast in colours present for sample B could indicate one of two things: either there is a stronger signal (more CuGaS\(_2\) phase) present in sample B than that of sample A, or it suggests a clearer distinction between regions of CuGaS\(_2\) growth and regions of uncovered substrate. SEM micrographs of these same regions (seen in Fig. 6.23 (a) and (b) for sample A and sample B respectively) show that numerous, smaller crystallites are present in regions between larger crystallites for
sample A in particular. Since the intensity mapping technique measures the relative intensity between a CuGaS$_2$ mode and the substrate mode, a more complete covering of the substrate by the CuGaS$_2$ phase (as in the case of sample A) would lead to a decrease in the colour contrast of Figs. 6.22 (a) and Figs. 6.22 (b).

![Figure 6.23](image_url)

**Figure 6.23.** SEM micrographs of sample A (a) and sample B (b). The marker indicates 10 μm.

Raman measurements were performed on an extremely Ga-rich epilayer (Cu: 6 at.%, Ga: 37 at.%, S: 57 at.%) using a line of 514.5 nm (Argon laser). This layer was grown over a period of 2 hours under a I/III ratio of 15 and a VI/(I+III) ratio of 11.9. The total carrier gas flow was 4.95 l/min. The measurement was made in the same standard region of the GaAs substrate analysed by other techniques (~1-2 mm from the leading edge).

Fig. 6.24 compares the three Raman spectra of sample C (top spectrum), sample A (middle spectrum) and a Ga$_2$S$_3$ thin film analysed by Julien et al. (1994) (bottom spectrum). The Raman lines present for sample C are noticeably different to those of sample A, which have already been discussed and identified as belonging to CuGaS$_2$. If one considers the significant difference between the compositions of either sample, then the difference in the spectra is not surprising. In the work of Julien et al. (1994), the authors compare the vibrational spectra of a series of Ga$_2$S$_3$ solid solutions with an increasing Cd content. The Ga$_2$S$_3$ atomic configuration can be treated in terms of a structural model based on a chemically ordered phase, whereby the GaS$_4$ tetrahedra are connected into a network through the twofold coordinated sulphur atoms. In order to maintain the correct ratio between the elements, one third of the S sites are vacant, which
also creates a distortion within the lattice. The symmetric GaS$_4$ molecule has four fundamental vibrational modes.

$$\Gamma = \Gamma_1 + \Gamma_3 + 2\Gamma_4$$

(6.3)

The sharp line of the Ga$_2$S$_3$ spectrum coincides with the breathing mode at 233 cm$^{-1}$. This mode is associated with the four neighbours of each S vacancy vibrating along the anion-vacancy bond direction.

\[ \text{Figure 6.24. Unpolarised Raman spectrum of an extremely Ga-rich sample of Cu}_x\text{Ga}_y\text{S}_z, \text{(top spectrum), an almost stoichiometric layer of CuGaS}_2 \text{ (middle spectrum), and a Ga}_2\text{S}_3 \text{ sample by Julien et al. (1994).} \]

The two $\Gamma_4$ modes are noticeable at 148 cm$^{-1}$ and 386 cm$^{-1}$, and the $\Gamma_5$ mode at 114 cm$^{-1}$. All other lines of this spectrum are associated with the A’ and T’ symmetries. In comparing the top spectrum (sample C) with this spectrum, one can make the following assignments: The dominant line at ~237 cm$^{-1}$ (E) matches well with the $\Gamma_1$ mode of Ga$_2$S$_3$ (reported at ~233 cm$^{-1}$). The two feint bands occurring at ~150 cm$^{-1}$ (D) and 395 cm$^{-1}$ (H) can be assigned to the two $\Gamma_4$ modes, whilst the weak line at ~116 cm$^{-1}$ (C)
can be assigned to the $\Gamma_5$ mode. The lines at $\sim 75$ cm$^{-1}$ (B) and 341 cm$^{-1}$ (F) are linked to the T' and A' symmetries of the GaS$_4$ tetrahedron respectively. The two broad bands at $\sim 361$ cm$^{-1}$ (G) and $\sim 415$ cm$^{-1}$ (I) are of unknown origin and are likely as a result of an additional phase associated with the presence of Cu in the sample.

We speculate that the 6 at.% Cu present in the sample is associated with the secondary phase, namely the ordered-defect compound (ODC) CuGa$_3$S$_5$. This would put 18 of the total 37 at.% Ga, and 30 of the total 57 at.% S as associated with this same phase. The remaining 19 at.% Ga and 27 at.% S needed to make up the full measure of the elements matches perfectly with the 2:3 ratio of the elements in the Ga$_2$S$_3$ phase already identified. Therefore, we tentatively assign the remaining two lines at $\sim 361$ cm$^{-1}$ and 415 cm$^{-1}$ to this ODC phase.

Raman intensity maps were performed over an equivalent area of sample C to the measurements performed for sample A and sample B. A single mapping was performed for this sample (see Fig. 6.25), whereby the relative intensity of the dominant line, which we assign to the breathing mode of the Ga$_2$S$_3$ phase, is compared to that of the GaAs LO line.

![Figure 6.25. Raman intensity map comparing relative intensity of the 237 cm$^{-1}$ line with that of the GaAs LO mode in sample C.](image-url)
Regions depicted in white indicate areas of maximum intensity, whereas darker regions depict areas of minimum intensity. There is little which can be conclusively determined from a single map, however, it is clear that the Ga$_2$S$_3$ phase occurs in large, isolated agglomerates.

In section 5.2.3, results from the EDS element mapping technique were presented (see Fig. 5.13). With this technique it was possible to identify the Cu and S-rich nature of the surface crystallites for that particular sample. The same technique was employed for this Ga-rich sample. Fig. 6.26 illustrates the distribution of the three elements Cu, Ga and S in the standard Region of Interest of the same sample described in Fig. 6.25. Measurements were performed using a 20 kV electron beam.

**Figure 6.26.** EDS mapping of sample C grown on GaAs at a temperature of 550 °C. A 20 kV image of the sample (a) illustrates the position of the secondary phase, whereas the distribution of Cu (b), Ga (c) and S (d) are given in yellow, green and red respectively. The marker indicates 10 µm.
From the distribution of elements it would appear that the crystallites are predominantly composed of Ga and S. Cu is clearly not present in these features and validates the suggestion that the Ga$_2$S$_3$ phase is responsible for the Raman lines observed in Fig. 6.24.

The sample areas measured by the Raman mapping technique are considerably larger than the areas represented by SEM in Fig. 6.23 and Fig. 6.26. This suggests that the regions of maximum intensity in Fig. 6.21, Fig. 6.22 and Fig. 6.25 comprise an accumulation of the crystallites seen in the SEM micrographs.

6.8 Summary

In conclusion, the structural properties of CuGaS$_2$ layers were described by XRD and TEM. Many secondary phases and structure types are possible, some of which were shown to have overlapping peaks in the simulated XRD spectra, which could create some confusion when identifying the phases present using this technique only. A comparison of XRD spectra for samples covering a wide range of Cu/Ga ratios in the solid illustrated that the 004 line (suggesting epitaxial growth) is dominant for samples with a Cu/Ga ratio less than ~0.84, whereas samples with a Cu/Ga ratio greater than ~0.84 exhibited predominantly polycrystalline growth, as deduced from the dominance of the 112 line. The formation of Cu$_x$S$_y$ and Ga$_x$S$_y$ phases were identified by the presence of additional lines in the XRD spectra for significantly Cu-rich and Ga-rich samples, respectively. The formation of Ga$_2$S$_3$ for a significantly Ga-rich layer was also identified by means of Raman spectroscopy. For one sample in particular, the disordered zincblende and CuPt polytypes of CuGaS$_2$ were identified by TEM, in addition to the chalcopyrite phase in the form of randomly orientated surface crystallites.

A careful study relating the position of the 004 line to that of the Cu/Ga ratio in the solid illustrated significant broadening of this line in addition to a shift to higher 2\(\theta\) values for samples with a Cu/Ga ratio in the solid of less than ~0.5. This shift was attributed to the formation of the ordered defect compound, CuGa$_3$S$_5$ for increasingly Ga-rich material.
An increase in substrate temperature resulted in a change in the growth mechanism from primarily $c$-axis orientated epitaxial growth to polycrystalline growth. This was attributed to an increase in the Cu/Ga ratio of the solid for higher growth temperatures. However, increased substrate degradation due to As desorption (illustrated by high resolution TEM) was also highlighted as a possible cause for this change in the growth mechanism. An increased likelihood of polycrystalline growth was also observed for layers grown using lower precursor concentrations due to an increased likelihood of substrate degradation.

It was shown that epitaxy was enhanced when GaAs substrates were submitted to the S-termination of the Ga dangling bonds prior to growth.
CHAPTER 7

RADIATIVE RECOMBINATION IN CuGaS$_2$

In this chapter, the optical properties as measured by photoluminescence (PL) spectroscopy will be presented. It will be shown that there are a number of typical transitions which are influenced by the growth conditions, composition of the solid, etc. The types of transitions and the conditions under which they are typically observed will first be presented. Thereafter, the typical behaviour of each of these transitions as a function of excitation energy and temperature will be considered.

The emphasis in this section is on thin films grown under a variety of conditions using the precursors Cu(hfac)$_2$Et$_3$N, TEGa, and DtBS. It was found that the PL obtained from these samples could be sub-divided into three energy regions: transitions which occur at ~2.49 eV (near band-edge PL), relatively narrow lines that occur between 2.4 eV and 2.3 eV, and low-energy luminescence occurring between 2.2 eV and 1.6 eV. The response from 5 epilayers displaying luminescence in each of these energy regions is depicted in Fig. 7.1. Near band-edge luminescence (seen in spectrum A) is typically fairly weak in relation to any lower-energy luminescence from the same sample. Luminescence from the green spectral region is typified by a transition occurring at ~2.4 eV although a transition at ~2.3 eV has been observed for Cu-rich material. These transitions are illustrated in spectrum B and spectrum C respectively. Broad bands of low-energy luminescence roughly centred at 2.2 eV, 1.8 eV and 1.6 eV have also been detected. The former two are illustrated by spectra D and E respectively. The 1.6 eV transition is uncommon, but is weakly observed in spectrum C. Each of these three energy regions will be discussed separately, and analysed in greater detail later in this chapter. Wherever possible, variable excitation power and variable temperature measurements were performed to identify the nature of each of these lines. To put these lines into context however, the typical transitions are first discussed as a function of the growth conditions and the measured compositions of the layers.
Figure 7.1 14 K PL spectra illustrating emissions from three different energy ranges corresponding to the green-blue, green, and orange-red spectral regions. Each spectrum typifies a transition from one of these regions. Samples were excited using the 457.9 nm line of an Ar+ laser.

7.1 Factors affecting the type of transitions observed

The type of transition(s) observed from a series of epilayers is understandably linked to the change in growth condition(s). This section will illustrate the PL dependence of a number of layers on changing I/III ratio (in the vapour and solid phase), changing VI/(I+III) ratio (in the vapour and solid phase), changing growth temperature, and changing precursor concentration.
7.1.1 Changing I/III ratio in the vapour phase

A series of layers were grown using the MO precursors: Cu(hfac)$_2$-Et$_3$N, TEGa and DtBS. The I/III ratio in the vapour phase was varied by changing the flow of the group III precursor. A VI/(I+III) ratio of 9 was used, and the substrate temperature of 550 °C was maintained during the 1 hour growth period. A total carrier gas flow of 4.95 l/min was used. Fig. 7.2 (a) depicts the PL obtained from a series of epilayers with a I/III ratio of 37, 42 and 47 in the vapour phase. Fig. 7.2 (b) depicts the PL in the near band-edge region between 2.53 eV and 2.44 eV.

**Figure 7.2**  
(a) A series of PL spectra for samples grown for 1 hour at 550 °C with varying I/III ratios in the vapour phase. The VI/(I+III) ratio during growth was kept at 9.0, and the total carrier gas flow was maintained at 4.95 l/min. Low temperature PL measurements were performed using a laser power of ~5.5 mW.  
(b) Near-band edge region of the same layers illustrated in (a).

Each of the three epilayers displayed in Fig. 7.2 is dominated by low-energy PL in the energy range of 2.3 eV to 2.1 eV. They also all exhibited luminescence centred at ~2.4 eV (labeled #2), which is the most intense for the samples grown with a I/III ratio in
the vapour phase of 37 and 47. The dominant line is centred at ~2.26 - 2.22 eV (labeled 
#3) for these samples, but is centred at ~2.16 eV (labeled #4) for the sample grown with a 
I/III ratio in the vapour phase of 42. Whilst it may be tempting to assume that lines #3 
and #4 are actually the same line, but shifted in accordance with the composition of the 
solid, it will be shown later in this chapter that these lines are due to different defects. 
Each of these layers exhibited extremely weak near-band edge luminescence, which can 
be seen on the high energy side of #2 in Fig. 7.2 (b).

The apparent lack of a trend in changes in the spectra as a function of increasing I/III 
ratio in the vapour phase is better understood when one considers the actual Cu/Ga ratio 
in the solid as measured by EDS. It has been shown (section 5.2.1) that small changes in 
the I/III ratio in the vapour phase do not always result in the expected change in the 
Cu/Ga ratio of the solid, when the composition of the solid is near-stoichiometric. Table 
7.1 lists the I/III ratio in the vapour phase and the composition of the solid phase for the 
layers described in Fig. 7.2.

<table>
<thead>
<tr>
<th>Vapour phase</th>
<th>In solid</th>
<th>Cu</th>
<th>Ga</th>
<th>S</th>
<th>Cu/Ga</th>
<th>S/(Cu+Ga)</th>
</tr>
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<tr>
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<td>Cu</td>
<td>Ga</td>
<td>S</td>
<td>Cu/Ga</td>
<td>S/(Cu+Ga)</td>
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<td>37</td>
<td>9</td>
<td>21.9</td>
<td>26.9</td>
<td>51.2</td>
<td>0.81</td>
<td>1.05</td>
</tr>
<tr>
<td>42</td>
<td>9</td>
<td>23.0</td>
<td>27.1</td>
<td>49.9</td>
<td>0.85</td>
<td>1.00</td>
</tr>
<tr>
<td>47</td>
<td>9</td>
<td>22.5</td>
<td>26.3</td>
<td>51.2</td>
<td>0.86</td>
<td>1.05</td>
</tr>
</tbody>
</table>

From the table it is tempting to ascribe the similarities in the PL of the layers with a I/III 
ratio of 37 and 47 in the vapour phase to the nominally identical S/(Cu+Ga) ratio in the 
solid. However, an inspection of the surface morphologies of these layers provides 
additional clues for the differences in the PL spectra. The smooth surface morphologies 
of these two layers suggest a lower Cu/Ga ratio in the solid in comparison to the sample 
grown with a I/III ratio in the vapour phase of 42. This latter sample exhibited distinct 
surface crystallites suggesting a slightly higher Cu/Ga ratio in the solid. Given the 
inherent uncertainty in the compositions obtained from EDS, it is tentatively assumed
here that the observed shift in the dominant transition from #3 to #4 (at lower energies) is due to an increase in Cu/Ga ratio in the solid. This is accompanied by a loss in the intensity of the higher-energy line #2. It is tenuous to speculate at this point, that a decrease in the Cu/Ga ratio of the solid leads to a dominance of the energy line (i.e. #3) since a change in the I/III ratio in the vapour phase consistently caused a change in the Cu/Ga and S/(Cu+Ga) ratios in the layers grown in this study.

Since changes in the I/III ratio in the vapour phase have an affect on both the Cu/Ga and S/(Cu+Ga) ratio of the solid, a series of PL spectra from a number of layers with a similar S/(Cu+Ga) ratio, but varying Cu/Ga ratio in the solid, is compared in Fig. 7.3. Each of the layers chosen for comparison in Fig. 7.3 were grown under similar conditions, i.e. growth temperature, growth time and total carrier gas flow. Only those layers with a near identical S/(Cu+Ga) ratio (~0.97) in the solid are compared in the figure. The solid composition is indicated on the graph.

It is evident that with an increasing Cu/Ga ratio in the solid, the dominant transition shifts from ~2.2 eV (labeled #3) to ~2.1 eV (labeled #4). A similar result was also reported by Bauknecht (1999) for CuGaSe$_2$ epilayers grown by MOVPE and Eberhardt et al. (2003) for CuGaS$_2$ epilayers grown by MBE. In the former study, Cu-rich material exhibited the strongest luminescence at approximately 1.62 eV. A second, higher-energy line at ~1.65 eV was observed for material with a slightly smaller Cu/Ga ratio in the solid. This higher-energy line dominated for lower Cu/Ga ratios in the solid and red-shifted by as much as 80 meV (accompanied by significant broadening and low-energy tailing) as the Cu/Ga ratio in the solid approached ~0.6. In the study by Eberhardt et al. (2003) the transition at ~2.1 eV shifted from 2.12 eV for Ga-rich material (Cu/Ga ratio = 0.91) to ~2.05 eV for Cu-rich material (Cu/Ga ratio = 1.82). In Fig. 7.3, the layer exhibiting a Cu/Ga and S/(Cu+Ga) ratio in the solid of 0.88 and 0.97 respectively, has a suggestion of two lines centred at ~2.19 eV and ~2.07 eV respectively (see arrows). However, these could not be resolved for any layer grown in this study owing to the broad nature of these bands and their significant overlap. The band labeled #4 for the Cu-rich sample (Cu/Ga ratio in the solid ~1.18) is centred at ~2.08 eV, which is significantly red-shifted from the
higher value of \( \sim 2.16 \text{ eV} \) characteristic to line #4 for slightly Cu-rich material. The broad nature of this band may be attributed to peak overlap between line #3 and line #4. However, the red-shift of \( \sim 80 \text{ meV} \) for this line in addition to the broad nature of this band is likely attributed to compensation within the semiconductor.

**Figure 7.3** A series of 15 K PL spectra for samples grown for 2 hours at 550°C with varying Cu/Ga ratios in the solid. All samples have a \( S/(Cu+Ga) \) ratio in the solid of \( \sim 0.97 \). Identical carrier gas flows (4.95 l/min) were used. Laser power \( \sim 10 \text{ mW} \).

Fig. 7.3 illustrates the shift in the position of the dominant line as a function of the Cu/Ga ratio in the solid. By applying a linear fit to this data (dashed line), a shift of \( \sim 34 \text{ meV} \) to lower energies is observed for every tenth of an increase in the Cu/Ga ratio in the solid.
7.1.2 Changing VI/(I+III) ratio in the vapour phase

In order to investigate the effect of a changing VI/(I+III) ratio on the optical response of CuGaS$_2$, a series of layers were grown for which the VI/(I+III) ratio in the vapour phase was varied by changing the flow of the group VI precursor. A I/III ratio of 28.2 was used, and the substrate temperature of 550 °C was maintained during the 2 hour growth period. A total carrier gas flow of 4.95 l/min was used. Fig. 7.4 depicts the PL obtained from a series of epilayers with a VI/(I+III) ratio of 7.07, 9.54 and 12.1 in the vapour phase. Fig. 7.4 (b) illustrates the weak PL obtained from each of these samples in the near band-edge region between 2.53 eV and 2.43 eV. Table 7.2 compares the I/III and VI/(I+III) ratios in the vapour phase with that of the Cu/Ga and S/(Cu+Ga) ratios in the solid.

<table>
<thead>
<tr>
<th>Vapour phase</th>
<th>In solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>I/III</td>
<td>V/(I+III)</td>
</tr>
<tr>
<td>28.2</td>
<td>12.1</td>
</tr>
<tr>
<td>28.2</td>
<td>9.54</td>
</tr>
<tr>
<td>28.2</td>
<td>7.07</td>
</tr>
</tbody>
</table>

In Fig. 7.4 (b), a shoulder is noticeable at ~2.48 eV for the samples grown with a VI/(I+III) ratio of 7.07 and 9.54 in the vapour phase. The intensity of this line is weak in each case and due to its close proximity to line #2, some uncertainty exists as to its exact position. The sample grown with the highest VI/(I+III) ratio displays little or no near band-edge PL.
From Table 7.2 a substantial decrease is noticed for the Cu/Ga ratio in the solid for the sample grown at the highest VI/(I+III) ratio in the vapour phase. The Cu-rich nature of this sample would explain the absence of any PL in the near band-edge region. It may be tempting to assign the dominant band of this layer to line #3 (typically present for Ga-rich material), but which has been visibly shifted to lower energies in the sample as a result of compensation (Bauknecht et al., 1999). However, it will be shown in the next section that regions of a different sample with a measured Cu/Ga ratio in the solid of between 0.82 and 0.75 exhibits little or no PL in this energy region. Rather, the PL is dominated in that sample by a broad band coinciding with the band labeled #5 at ~1.8 eV. Whilst the XRD analysis of the layer grown with a VI/(I+III) ratio in the vapour phase of 12.1 indicates c-axis orientated CuGaS$_2$, there is a faint suggestion of the secondary phase, GaS. Aydinli et al. (2000) describes the PL properties of bulk GaS grown by a modified Bridgman method. In that study, three typical bands were observed at low temperature,
centred at ~2.22 eV, ~2.02 eV and ~1.59 eV. It may be possible, therefore, that the 2.2 eV PL band exhibited in the top spectrum of Fig. 7.4 (a) originates from a GaS phase instead of CuGaS$_2$. However, since the XRD peak attributed to the GaS phase is very weak, it is unlikely that the dominant PL band can be ascribed to this phase. Instead, it is far more likely that the broad nature of this band, in addition to the significant red-shift relative to the energy at which this line is usually measured (~2.22 eV) for slightly Ga-rich material can be ascribed to compensation in the semiconductor. Material with a Cu/Ga ratio of this order (~0.70) usually only exhibits luminescence at ~1.8 eV. This result (luminescence of ~2.2 eV) is considered atypical for material of this composition.

Line #2 (~2.4 eV) is clearly the most intense in the sample grown with a VI/(I+III) ratio of 9.54 in the vapour phase. This is likely owing to the close proximity of the Cu/Ga ratio in the solid to that of the ideal value (which is at a measured value of ~0.84). It will be shown in the next section that line #2 is the most intense for samples which are near-stoichiometric in composition. The broad band of red PL, labeled #5 is seen to increase in intensity with a decrease in the Cu/Ga ratio of the solid.

7.1.3 Changing Cu/Ga and S/(Cu+Ga) ratio within a single layer

In section 5.1, the variations in the Cu, Ga and S-content of the solid across a single CuGaS$_2$ thin film deposited on a Si substrate were presented. In this section the influence of the Cu/Ga and S/(Cu+Ga) ratios in the solid on the PL spectra of this same layer are described in detail. Fig. 7.5 illustrates the variation in the Cu/Ga and S/(Cu+Ga) ratios across the substrate surface. These variations across the substrate surface were described in section 5.1. As expected, the Cu/Ga profile in Fig. 7.5 (a) is similar in appearance to the profile for the Cu-content illustrated in Fig. 5.2 (a); and the S/(Cu+Ga) profile is comparable to that of the S-content illustrated in Fig. 5.2 (c).
Figure 7.5. Inhomogeneities in composition across the layer discussed in section 5.1 are plotted as a variable Cu/Ga ratio (a) and variable S/(Cu+Ga) ratio (b) in the solid. Directions along which a series of PL scans were performed are indicated by means of the arrows in (a), namely A to C, D to F, A to D, and B to E.
A series of PL spectra (see Fig. 7.6 (a)) were recorded along a line from the area marked A to the area marked C as indicated in Fig. 7.5 (a). EDS measurements taken in the direction indicated, reveal an incremental decrease in the Cu/Ga ratio and increase in the S/(Cu+Ga) ratio in the solid. This change in composition is accompanied by a decrease in the intensity of the dominant line, labeled #4 for Cu-rich material and the emergence of line #3 (typical for Ga-rich material) for Cu/Ga ratios between 0.91 and 0.85. Any further decrease in the Cu/Ga ratio results in the disappearance of the lines above 2 eV in favour of broad, lower-energy luminescence centred at ~1.85 eV (#5). In addition to changes in the relative intensities of lines #3 and #4, there is a relative increase in the intensity of line #2 to a maximum for a Cu/Ga ratio of 0.91; this line diminishes for a further decrease in the Cu/Ga ratio of the solid.

![Figure 7.6](image)

Figure 7.6. (a) A series of 2 K PL spectra recorded in a line from the region marked A (top spectrum) to the region marked C (bottom spectrum) in Fig. 7.5. Measurements were taken ~2 mm apart. (b) A similar series of low temperature PL spectra recorded in a line from the region marked D (top spectrum) to the region marked F (bottom spectrum) in Fig. 7.5. Measurements were taken ~4 mm apart. The Cu/Ga and S/(Cu+Ga) ratios in the solid are indicated alongside each spectrum.
To confirm these observations, similar measurements were taken (see Fig. 7.6 (b)) further away from the leading edge of the substrate in a straight line from the region marked D to the region marked F in Fig. 7.5 (a). In a similar fashion to that which was seen in Fig. 7.6 (a), the dominant transition changes from #4 (Cu/Ga $\approx 0.92$) to #3 (Cu/Ga $\approx 0.84$) as the layer becomes progressively Ga-rich. Regions of the sample with a Cu/Ga ratio less than 0.84 exhibited PL from line #5 only.

**Figure 7.7.** (a) A series of 2 K PL spectra recorded in a line from the region marked A (bottom spectrum) to the region marked D (top spectrum) in Fig. 7.5 (a). (b) A series of low temperature PL spectra recorded in a line from the region marked B (bottom spectrum) to the region marked E (top spectrum) in Fig. 7.5 (a). The Cu/Ga and S/(Cu+Ga) ratios in the solid are indicated alongside each spectrum.

Further measurements were taken in a line linking regions A and D illustrated in Fig. 7.5 (a). These spectra are depicted in Fig. 7.7 and the Cu/Ga and S/(Cu+Ga) ratios as measured by EDS are listed alongside each spectrum. Each of the spectra illustrated are from Cu-rich areas of the sample and as such the dominant transition in each of the spectra can be assigned to that of the transition labeled #4. Despite a relatively large change in the Cu/Ga ratio of the solid (in addition to the concomitant change in the
S/(Cu+Ga) ratio of the solid) for each of the areas analysed, there is no apparent shift in the position of line #4.

A similar series of measurement were performed in a line from the leading edge toward the trailing edge (see B to E in Fig. 7.5 (a)) and these spectra are illustrated in Fig. 7.7 (b). This region was nearer to the stoichiometric Cu/Ga ratio in the solid than along line A to D. It is evident from the position of the dominant line (~2.24 eV) that this can be assigned to the transition typical for Ga-rich material. In addition, line #2 is significantly more intense for these compositions than for the Cu-rich material illustrated in Fig. 7.7 (a).

To conclude this section, it will be shown how compensation within the semiconductor cannot account for the large shift in the dominant transition from ~2.1 eV in Cu-rich material to ~2.25 eV in Ga-rich material. Bauknecht (1999) described how the half-width at half-maximum (HWHM), on the high energy side of the line ascribed to a so-called “quasi” D⁰A¹ pair recombination in compensated material increased with decreasing Cu/Ga ratio in the solid, which was then attributed to greater degrees of compensation. In order to establish whether compensation plays a role in the observed shift of the dominant PL lines above 2 eV, the HWHM of lines #3 and #4 displaying little overlap with line #2 in spectra taken from the sample described above, have been measured and plotted as a function of the observed peak position in Fig. 7.8. One would expect an increase in the HWHM as a function of decreasing peak energy if indeed compensation played a role, due to a larger degree of fluctuations in the band edges. The opposite result was found, however, and an increase in HWHM was accompanied here by an increase in peak energy.
Figure 7.8. Dependence of HWHM on peak energy for all lines labeled #3 and #4 in the PL spectra displayed in Fig. 7.6 and Fig. 7.7 (a).

7.1.4 Growth temperature

To investigate the effect of growth temperature on the optical properties of CuGaS$_2$ thin films, a series of epilayers was grown for 2 hours at temperatures of 550 °C, 575 °C and 600 °C. The total flow of carrier gas was maintained at 4.95 l/min and a I/III ratio and VI/(I+III) ratio of 28.2 and 7.1 in the vapour phase, respectively, were used. Fig. 7.9 depicts the 14 K spectra for each of these epilayers grown heteroepitaxially on GaAs(001) substrates at the temperatures indicated.

The Cu/Ga ratio in the solid for the layer grown at 550 °C suggests Ga-rich material, whereas the Cu/Ga ratio in the solid for the layer grown at 575 °C suggests Cu-rich material. The position of the dominant line in the spectrum of the former layer (~2.2 eV) matches well with the expected position of line #3, whereas the position of the dominant
line in the spectrum of the sample grown at 575 °C (~2.15 eV) matches well with the expected position of line #4.

![Figure 7.9](image)

**Figure 7.9** A series of 14 K PL spectra for samples grown for 2 hours with a I/III ratio and VI/(I+III) ratio of 28.2 and 7.1 in the vapour phase, respectively. The total carrier gas flow was maintained at 4.95 l/min. Laser power ~11 mW.

The spectrum for the layer grown at 600 °C is extremely weak in comparison to the layers grown at lower temperatures and appears entirely different. The decrease in the optical quality of this layer is likely related to a change in the composition of the solid. It was shown in section 5.2.3 that an increase in substrate temperature led to a decrease in the available S at the growth interface. This in turn led to a decrease in the amount of Cu incorporated into the CuGaS$_2$ lattice and an accumulation of a Cu-rich phase on the surface. Changes in the optical properties of grown epilayers are therefore as a result of changes in the Cu/Ga ratio of the underlying epilayer, which are brought about by changes in the substrate temperature during growth.
7.1.5 Precursor concentrations

To investigate the effect of the precursor concentration on the optical quality of the grown epilayers, the same layers discussed in section 6.4.2 were analysed by PL. Changes to the precursor concentrations were brought about by halving the molar flows for the Cu, Ga and S precursors, and doubling the growth time to compensate for the expected drop in the growth rate.

![Figure 7.10](image)

**Figure 7.10** 14 K PL spectra for two samples grown with different reagent concentrations during growth. The growth time was doubled for the sample grown with the reagent concentrations halved. The I/III ratio and VI/(I+III) ratio was maintained at 37 and 9 respectively during growth. The total carrier gas flow was maintained at 4.95 l/min. Low temperature PL measurements were performed using a laser power of ~9 mW.

Fig. 7.10 illustrates the effect of reagent concentration on the PL spectra of the grown epilayers. The PL of the layer grown for 2 hours with half the reagent concentration is
almost identical to the PL of the initial layer. This illustrates that the growth rate has a negligible effect on the optical quality of the grown epilayers. In section 6.4.2 the structural properties of these two layers were discussed. It was shown that by halving the precursor concentration during growth (i.e. halving the growth rate) and doubling the growth time, the CuGaS$_2$ layer no longer grew in an epitaxial manner, but that probably due to substrate degradation, polycrystalline growth resulted. This suggests that the optical properties of epitaxial thin films and polycrystalline thin films are essentially the same.

7.2 Behaviour of individual transitions

In the following section, each of the lines observed for the thin films grown in this study are analysed in terms of variable temperature and excitation power measurements. These measurements will provide insight into the nature of these transitions and their possible origins.

7.2.1 Near band-edge photoluminescence

The near band edge luminescence is typically weak in comparison to the lower-energy PL for all layers grown in this study. Fig. 7.11 illustrates the difference in the PL spectra obtained from both a slightly Ga-rich and a Cu-rich sample of CuGaS$_2$/GaAs(001). Both spectra are dominated by yellowish PL assigned to the transitions labeled #3 and #4 occurring at 2.195 eV and 2.098 eV respectively. Green PL (#2) is observed for the Ga-rich sample only. Near band-edge luminescence (#1) is observed in both samples (see inset of Fig. 7.11), however, since there is significant peak overlap with the 2.4 eV line in the Ga-rich sample, the near band edge luminescence is better resolved for the Cu-rich layer.
Figure 7.11  Typical 14 K PL spectra for Cu-rich (grey) and Ga-rich (black) samples with similar $S/(Cu+Ga)$ ratios in the solid. Layers were grown at 550 °C on GaAs substrates for a period of 2 hours with a total carrier gas flow of 4.95 l/min. Laser power ~9 mW.

The peak position of the high energy line (#1) measured for the Ga-rich layer shows little dependence on the excitation power as seen in Fig. 7.12 (a). Each spectrum has been normalized to the maximum intensity of line #1 and shifted vertically for clarity. The dependence of the integrated emission of this line on excitation intensity is given as a double logarithmic plot in Fig. 7.12 (b). Also included in this figure is the equivalent data measured for the Cu-rich layer discussed in Fig. 7.11.

If this line is excitonic in nature, its intensity should be directly proportional to the number of excitons, which in turn depends on the number of electrons and holes in the conduction and valence bands respectively. An equal number of electrons and holes are created in direct proportion to the incident excitation rate and therefore the emission
intensity of free-excitons ideally exhibits a quadratic dependence on laser power. Any bound excitons are in thermal equilibrium with free-excitons and should display a near-identical dependence on laser power. Schmidt et al. (1992) showed that the exponent $k$ in the relationship between PL intensity $I$, and the laser power $P_{\text{laser}}$: $I = P_{\text{laser}}^k$, is generally $1 < k < 2$ on condition that the energy of the laser light exceeds the band gap of the material by a sufficient amount. If the energy is tuned to the excitonic band gap energy, then $k$ generally equals 1. This linear dependence of a double logarithmic plot of integrated emission versus laser power is only observed in the Cu-rich layer ($k = 1.0$). The Ga-rich layer, however, exhibited a superlinear dependence ($k = 1.4$) despite using the same energy for excitation.

![Figure 7.12](image)

**Figure 7.12**  
(a) Excitation intensity dependence of the PL for a Ga-rich sample in the near-band edge region. (b) Double logarithmic plot of the integrated intensity of line #1 with respect to excitation intensity for the Cu-rich layer on GaAs substrate (solid square), Ga-rich layer on GaAs substrate (open squares).

The temperature dependent PL of the same Cu-rich and slightly Ga-rich layers discussed in Fig. 7.12, at a constant excitation power, is illustrated in Fig. 7.13. In each of these
series of spectra, line #1 can be observed throughout the whole temperature range. This band of PL cannot be further resolved and has therefore been treated as a single transition. The maximum of this line in the slightly Ga-rich sample is shown to shift from 2.479 eV at low temperatures, to 2.438 eV at room temperature (41 meV). For the Cu-rich layer, a shift in this line is observed from 2.481 eV to 2.446 eV over the same temperature range (35 meV). A possible reason for the smaller shift for the slightly Cu-rich layer may be the participation of non-radiative recombination feeding into the excitonic recombination. The energy of this line is the same for Cu-rich and Ga-rich samples at low temperatures. If this line is excitonic in origin then this result suggests that the band gap of the material is unaffected by changes in composition, a result which was also reported by Binsma et al. (1982a) for the luminescence of CuInS$_2$. An acceptor-bound exciton A$^0$X at 2.489 eV was reported by Metzner et al. (2004) for MBE-grown CuGaS$_2$, whereas Shirakata and Chichibu (2000) reported a free-excitonic peak at 2.489 eV and a bound excitonic peak at 2.477 eV for LP-MOVPE grown material. Previous work by our group (Botha et al., 2001) reported on two bound-excitonic lines at 2.493 eV and 2.486 eV for Cu-rich layers of CuGaS$_2$ epilayers grown by vacuum deposition. The position of the excitonic line occurring for both Cu-rich and Ga-rich epilayers in this study therefore coincides with previously published work.

The peak energies for each of these series of spectra have been plotted as a function of temperature in Figs. 7.14 (a) and (b) respectively. Excitonic transitions will generally follow the temperature dependence of the band gap, $E_g$. The reported temperature dependence of the A-exciton of bulk material is illustrated in both Fig. 7.14 (a) and Fig 7.14 (b) (Shirakata and Chichibu, 2000). The temperature dependence of line #1 for both Cu-rich and Ga-rich material in this study follow the expected temperature dependence of the band gap, therefore implying that the transition is excitonic in nature. This relationship has been described by two different models, namely the Varshni model and the Bose-Einstein model. The Varshni model (Varshni, 1967) estimates the reduction of the band gap with temperature by the equation:
\[ E_g(T) = E_g(0) - \frac{\alpha T^2}{(\beta + T)} \]  \hspace{1cm} (7.1)

where \( E_g(0) \) denotes the band gap at 0 K, \( \alpha \) is a constant, and \( \beta \) is an undefined temperature parameter.

Figure 7.13  Normalised temperature dependent PL in the near-band edge region for a Cu-rich layer (a) and slightly Ga-rich layer (b) on GaAs substrates.

The Bose-Einstein model (Pässler, 2001) can be represented by the equation:

\[ E_g = E_g(0) - \kappa \frac{\Theta_E}{\exp\left(\frac{\Theta_E}{T}\right) - 1} \]  \hspace{1cm} (7.2)

where \( E_g(0) \) denotes the band gap at 0 K, \( \kappa \) is a constant, and \( \Theta_E \) is the Einstein characteristic temperature.
Figure 7.14  Position of the excitonic line (#1) with respect to temperature for the Cu-rich layer (a) and Ga-rich layer (b). Two models were used to fit the experimental data and obtain a $E_g$ at 0 K. The Varshni model is represented by the dotted line, whereas the Bose-Einstein model is represented by the dashed line.

Both of these models were applied to the temperature dependence of this line for both the Cu-rich and Ga-rich samples. The Bose-Einstein model (dotted, grey curve) clearly offers a better fit to the data points, especially at lower temperatures, than the Varshni model (dashed, black line), which does not simulate the band gap of several types of semiconductors at cryogenic temperatures (Viña et al., 1984). Fitting parameters and temperature coefficients for the Bose-Einstein model are summarized in Table 7.3. The Varshni model calculated a band gap of 2.482 eV for both the Cu-rich and Ga-rich materials, but the parameters were not uniquely defined and have been excluded from Table 7.3.

The decrease in intensity of line #1 with temperature is shown in Fig. 7.15 for both the Cu-rich and Ga-rich samples. An estimation of the binding energy, $\varepsilon$ of the exciton can be obtained from an Arrhenius plot of this data. Often, a good approximation of this binding energy can be obtained by calculating the gradient in the high temperature region of a $\ln I$ versus $1/T$ graph, and equating this with $\varepsilon/k$, where $k$ is the Boltzmann’s constant. However, a more accurate approximation can be obtained by using the relationship
\[ I = \frac{I_0}{1 + C \exp^{\frac{\kappa}{T}}} \]  

(7.3)

where \( I_0 \) is the integrated intensity when \( T \) approaches 0 K and \( C \) is a temperature-independent constant related to the Fermi level (Binsma et al., 1982a).

**Table 7.3.** Parameters for the Bose-Einstein temperature dependence of the excitonic transition at ~2.48 eV for both the Cu-rich and Ga-rich samples.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bose-Einstein model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu-rich</td>
</tr>
<tr>
<td>Energy</td>
<td>( 2.481 \pm 1.4 \times 10^{-3} ) eV</td>
</tr>
<tr>
<td>( \kappa )</td>
<td>( 0.197 \pm 17.5 \times 10^{-3} )</td>
</tr>
<tr>
<td>( \Theta_E )</td>
<td>( 544 \pm 21.0 ) K</td>
</tr>
</tbody>
</table>

**Figure 7.15** Arrhenius plot of the integrated emission of the excitonic line (#1) with respect to temperature for the Cu-rich layer (a) and the slightly Ga-rich layer (b).

The resulting parameters obtained from these fits are listed in Table 7.4. A binding energy of ~32 meV is observed for the Cu-rich layer, which resembles the value of 28 meV for the binding energy of the exciton in bulk CuGaS\(_2\) (Shirakata and Chichibu, 2000). The same group reported a value of 29 meV for the binding energies of the F-X transition, and 12 meV for the B-X transition. The binding energy of the F-X transition has been reported to be 28-29 meV by Tell and Kasper (1973). The binding energy calculated for the Ga-rich layer in this work is 15 meV, which is significantly lower than
that of the Cu-rich layer. Shirakata and Chichibu (2000) reported binding energies of 29 meV and 12 meV for the F-X and B-X, respectively.

Table 7.4 Parameters obtained by fitting Eq. 7.3 to the temperature dependence of the integrated emission intensity of line #1 for a Cu-rich sample and slightly Ga-rich sample.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cu-rich</th>
<th>Ga-rich</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>5.99 ± 1.56</td>
<td>9.69 ± 2.32</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>32.1 ± 4.2 meV</td>
<td>14.6 ± 1.8 meV</td>
</tr>
</tbody>
</table>

Fig. 7.16 illustrates the temperature dependence of the band-edge luminescence for a near-stoichiometric thin film grown on a Si(001) substrate at 550 °C for a period of two hours. The Cu/Ga ratio in the solid was determined from EDS to be ~0.84. From the series of spectra in Fig. 7.16, a clear blue-shift is observed for this line (centred at 2.480 eV at 15 K) for temperatures below 90 K. Thereafter the line red-shifts in accordance with the Bose-Einstein relationship as described previously. The shift in the peak position as a function of temperature is illustrated in Fig. 7.17. A total shift of ~21 meV is observed over the entire temperature range. After applying the Bose-Einstein relationship to the experimental data for this sample, a value of 2.486 eV was obtained for the band gap at 0 K. A larger band gap (~6 meV) is calculated for this layer than that which was calculated for the layers grown on GaAs substrates. This difference in peak position possibly originates from the lattice mismatch strain present in the interfacial region of CuGaS$_2$/GaAs(001) epitaxial layers shifting the fundamental band gap to a lower energy than the unstrained crystal.
Figure 7.16  Temperature dependent PL in the near-band edge region for a near-stoichiometric layer grown on a Si substrate.

Figure 7.17  Position of the excitonic line (#1) with respect to temperature for the near-stoichiometric layer grown on a Si substrate. The Bose-Einstein fit is represented by the dashed line.
The anomalous behavior of the peak position at low temperature (i.e. the observed blue-shift at lower temperatures), which can also be seen for the slightly Ga-rich layer grown on GaAs (see Fig. 7.14 (b)) has been ascribed to two possible mechanisms: the first (Shay and Wernick, 1975) details the behavior of the band gap on the basis of the temperature dependant $p$-$d$ hybridisation. The band gap of the I-III-VI$_2$ chalcopyrites is known to be lowered with respect to the corresponding II-VI binary analogues as a result of the hybridization of the copper $d$-levels and the sulphur $p$-levels. An increased proportion of $d$-character in the uppermost valence band results in an increased downshift in the band gap energy. An increasing temperature leads to a larger inter-atomic spacing, which correspondingly decreases the effective $p$-$d$ hybridization. The initial increase in band gap energy with larger temperatures is as a result of this mechanism being the most dominant. A further increase in temperature results in the normal decrease in energy by decreasing ionicity and Urbach tailing, however, this decrease is not as severe as a result of the former mechanism. The second explanation for the increasing peak position at lower temperatures is given by Bauknecht et al. (2000a). In that study it was shown how the B-X transition for epitaxial CuGaSe$_2$ is significantly more temperature dependent than the F-X transition and the dominant recombination mechanism changes from B-X to F-X (an observation which was also reported on by Chichibu et al. (1994) and Yamada et al. (1996)). As a result there is an inversion in the B-X/F-X intensity ratio with increasing temperature. Due to the lower energy of the B-X transition, the centre of the peak position in the case of unresolved F-X and B-X transitions, is seen to shift to higher energies as the F-X transition becomes more dominant at higher temperatures. Eq. 7.3 was applied to the Arrhenius relationship of the integrated intensities of this peak and a thermal binding energy of 14.8 ± 4.3 meV was calculated. This value matches with the value obtained for a slightly Ga-rich layer grown epitaxially on GaAs(001), discussed earlier.

7.2.2 Green photoluminescence at ~2.4 eV

The second energy region in which PL is commonly observed occurs in the green part of the visible spectrum. Spectrum B of Fig. 7.1 typifies the PL observed from these layers.
Eberhardt *et al.* (2003) reported two free-to-bound (F-B) transitions at 2.435 eV and 2.412 eV, respectively, and one donor-acceptor (D$^0$A$^0$) transition at 2.40 eV for Cu-rich CuGaS$_2$ grown by MBE, which was excited with a similar laser intensity and measured at a temperature comparable to that used in the present work. Choi *et al.* (1996) described a transition occurring at ~2.35 eV (also attributed to a D$^0$A$^0$ pair recombination) for bulk CuGaS$_2$ samples grown by the horizontal Bridgman method. Chichibu *et al.* (1997) reported a weak transition occurring at ~2.4 eV at low temperatures, but made no attempt to describe it and instead concentrated on describing only the excitonic PL. Shirakata and Chichibu (2000) investigated the PL obtained from CuGaS$_2$ epilayers grown by MOVPE on both GaP and GaAs substrates in terms of the normal-tripropylgallium (TPGa) flow rate and resulting composition of the solid. In that study the line occurring at 2.427 eV (seen only in stoichiometric and Cu-rich epilayers) was attributed to a F-B transition, whilst a line occurring at 2.40 eV for layers analysing as Ga-rich was ascribed to a D$^0$A$^0$ transition. Ooe *et al.* (1991) has investigated the influence of Zn-doping on the PL spectra of CuGaS$_2$ crystals prepared by the iodine transport method. Undoped samples analysed by this group exhibited strong PL in the 2.4 eV region, but a new transition increasingly dominated at lower energies as the Zn-dopant increased. This new transition occurred at 2.315 eV for $x = 0.0005$ in the crystals produced from the starting material (CuGaS$_2$)$_{1-x}$ -(2ZnS)$_x$. The lower-energy peak was attributed to D$^0$A$^0$ pair recombination between the Zn$_{Cu}$ antisite and either the V$_{Ga}$ or the Zn$_{Cu}$-V$_{Ga}$ complex. Massé (1985) studied a peak occurring at 2.39 eV in some detail and attributed it to D$^0$A$^0$ pair recombination. The acceptors were assigned to either cation vacancies or S interstitials. The binding energies of the donor and acceptor were reported to be of the order of ~50 meV and ~130 meV respectively.
Fig. 7.18  
Excitation intensity dependence of the green PL (line #2) for a Cu-rich (a), and two Ga-rich layers (b), (c). These layers have been labeled A, B and C respectively, for convenience. All samples displayed similar S/(Cu+Ga) ratios in the solid. Sample A has been plotted on a semi-log scale for clarity.

To illustrate the temperature and excitation intensity dependence of line #2 occurring at ~2.4 eV, three samples were chosen representing different Cu/Ga ratios in the solid (Fig. 7.18). Table 7.5 lists the growth conditions and compositions of these samples. The 2.4 eV PL was significantly weaker in the Cu-rich layer (sample A) than in either of the Ga-rich layers (sample B and sample C). The series of spectra for both sample B and sample C are nearly identical, which is attributed to the similarities in their composition. For each of the samples, this band disappears almost completely at very low excitation intensities.

Table 7.5  
Parameters of three samples displaying PL in the 2.4 eV range. All samples were grown using the copper and sulphur precursors, \(\text{Cu(hfac)}_2\cdot\text{Et}_3\text{N}\) and DtBS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Figure</th>
<th>Growth temp.</th>
<th>Gallium precursor</th>
<th>Growth time</th>
<th>I/III in vapour</th>
<th>VI/(I+III) in vapour</th>
<th>Cu/Ga in solid</th>
<th>S/(Cu+Ga) in solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Fig. 7.18 (a)</td>
<td>550 °C</td>
<td>TMGa</td>
<td>2 hours</td>
<td>14.9</td>
<td>11.8</td>
<td>1.29</td>
<td>1.02</td>
</tr>
<tr>
<td>B</td>
<td>Fig. 7.18 (b)</td>
<td>550 °C</td>
<td>TEGa</td>
<td>1 hour</td>
<td>37</td>
<td>9</td>
<td>0.85</td>
<td>1.00</td>
</tr>
<tr>
<td>C</td>
<td>Fig. 7.18 (c)</td>
<td>550 °C</td>
<td>TEGa</td>
<td>1 hour</td>
<td>42</td>
<td>9</td>
<td>0.81</td>
<td>1.05</td>
</tr>
</tbody>
</table>
Fig. 7.19 (a) Double logarithmic plot of the integrated intensities of line #2 for each of the series of spectra displayed in Fig. 7.18. (b) Positions of these lines plotted as a function of excitation intensity.

Fig. 7.19 (a) depicts a double logarithmic plot of the intensity of the 2.4 eV peak as a function of excitation intensity. From this relationship a superlinear behaviour of the emission intensity versus laser power is obtained. The gradients of 1.1 and 1.2 obtained for the Ga-rich epilayers can be considered identical within experimental error. However, the integrated intensities of this peak for the Cu-rich layer (open stars) increases slightly faster with laser power ($k \approx 1.3$). Shirakata et al. (1990) reported a much higher rate of increase in the intensity of the 2.4 eV line as a function of excitation intensity ($k = 1.7$) occurring at 77 K for crystals grown by the iodine-transport (IT) method; however, no such relationship was observed at lower temperatures. Metzner et al. (2004) measured a sublinear behaviour for two $D^0A^0$ lines occurring at 2.411 eV and 2.391 eV for Cu-rich material grown by MBE. Shirakata and Chichibu (2000) reported a superlinear behaviour ($k = 1.16$) for the peak at 2.4 eV for MOVPE-grown CuGaS$_2$/GaP.

Clearly there is some discrepancy in the reported laser power dependence of PL in this region. It is possible that electrons from non-radiative combinations feed into this radiative transition at higher laser powers thereby leading to a superlinear behaviour of the PL intensity with respect to laser power. This possibility highlights the complexity of this material.

To further characterise this transition, the peak energy as a function of excitation intensity is plotted in Fig. 7.19 (b). It should be noted that there is a distinct difference in the peak
energy between Ga-rich (~2.38 eV) and Cu-rich material (~2.32 eV). This has been observed in earlier studies in our laboratory (Botha et al., 2001) for CuGaS$_2$/GaAs grown by vacuum deposition. In this earlier work, the PL of Cu-rich material was dominated by a line attributed to a D$^0$A$^0$ transition at 2.3 eV, whilst Ga-rich material typically exhibited a different line centred at ~2.4 eV. It was proposed that the change in the Cu/Ga ratio of the solid led to a change in the dominant acceptor involved in this transition, whereas the shallower donor remained common to both Cu-rich and Ga-rich material. In the event that the transition involves the same set of defects for both Cu-rich and Ga-rich material, the shift from ~2.3 eV to ~2.4 eV for a decreasing Cu/Ga ratio in the solid can also be explained as follows: The recombination energy of a D$^0$A$^0$ pair can be given by the well-known equation (Pankove, 1971):

$$h\nu = E_G - (E_A + E_D) + \frac{e^2}{4\pi\epsilon r}$$  (7.4)

where $E_G$ is the band gap, $r$ is the separation between impurities and $e^2/4\pi\epsilon r$ is a Coulomb term. A common defect inherent to this class of materials is the cation antisite (Zhang et al., 1998). The Ga$_{cu}$ antisite would be common in Ga-rich materials and a decrease in the Cu/Ga ratio would lead to an increase in the density of this defect. With an increase in the number of these defects, the separation between them decreases. This would lead to an overall increase in the energy of the D$^0$A$^0$ transition in accordance with Eq. 7.4. It may be proposed that the transitions occurring at ~2.3 eV and ~2.4 eV for Cu-rich and Ga-rich material respectively are identical in origin yet shift in energy as a function of the composition of the solid.

A clear blue-shift in this emission is observed for the Ga-rich layers as the excitation intensity increases. Sample B and C exhibit a shift of 4.6 and 5.7 meV/decade change in the excitation intensity, respectively. From the work of Shirakata and Chichibu (2000) our group estimates that the peak reported at 2.4 eV undergoes a shift of ~4 meV/decade change in excitation intensity. This blue-shift with increasing laser power is typical for a D$^0$A$^0$ type transition.
In Fig. 7.20 the temperature dependence of the PL spectra is shown for both the Cu-rich sample (sample A) and one of the Ga-rich samples (sample C). As previously described, line #2 is significantly less intense for the Cu-rich sample; however, it is clear from the change in the shape of the spectra, that this line is rapidly quenched at temperatures exceeding 45 K. This trend is clearer in sample C where this line rapidly quenches between the temperatures of 20 K and 110 K. This rapid quenching suggests the involvement of a relatively shallow level in the transition.

![Fig. 7.20](image)

**Fig. 7.20** Temperature dependent PL plotted on a semi-logarithmic scale highlighting the green PL (line #2) for a Cu-rich layer (a) and plotted on a linear scale for one of the Ga-rich layers - Sample C (b). Laser power 5.4 mW.

An Arrhenius plot of the integrated intensities (obtained from curve fitting) of this transition for both samples is shown in Fig. 7.21 (a). Due to large peak overlap, it was not possible to obtain a thermal activation energy for sample A (open squares); however, a straight line fit has been applied to the high temperature measurements of sample C and an activation energy of \( \sim 27 \text{ meV} \) was obtained. Massé (1985) reported a donor binding energy of 50 meV and an acceptor binding energy of 130 meV. Choi *et al.* (1996)
described an activation energy of 11 meV for a similar line occurring at this energy and attributed it to the binding energy of the donor. Shirakata and Chichibu (2000) described an acceptor and donor level at 100 meV and 46 meV respectively, whereas Metzner et al. (2004) suggested a donor level at 25 meV. In previous work by our group it was speculated that a donor with a binding energy of ~53 meV exists. Therefore the activation energy of ~27 meV for this pair emission is close to the reported values for a shallow defect, possibly a donor.

![Figure 7.21](image)

**Figure 7.21** Arrhenius plot of the integrated intensities of line #2 with respect to temperature (a). The positions of these lines are plotted with respect to temperature in (b).

Fig. 7.21 (b) illustrates the influence of temperature on the energy of this transition. Line #2 in both the Cu-rich and Ga-rich samples exhibit a red-shift with an increase in temperature and the complete thermal quenching of this peak occurs at temperatures below 70 K. Metzner et al. (2004) ascribed an apparent blue-shift in this line to the thermal ionization of the shallower level (donor at ~25 meV) which will enhance a related F-B transition occurring at 2.415 eV. According to Binsma et al. (1982b), an increase in temperature results in the migration of mobile charge carriers to more favourable sites (i.e. smaller pair separations $r$ - see Eq. 7.4), resulting in a blue-shift of $D^0A^0$ transitions in addition to the expected shift in band gap. The band gap, however, is only expected to shift to lower energies for a temperature greater than ~90 K, therefore the red-shift observed for this line at higher temperatures is as a result of some other mechanism. Dean (1982) describes a mechanism which may explain the red-shift
observed for this line with increasing temperature. In that study, an opposing shift in a $D^0A^0$ line can occur depending on the difference in ionisation energy between the neutral donor and neutral acceptor involved. If the ionisation energy of the shallower defect is significantly smaller than the ionisation energy of the deeper defect, the ionised shallower level will reduce the ionisation energy of the deeper level by an amount related to the Coulombic factor. The important factor here is whether the ionisation energy of the reduced level is less than the ionisation energy of the shallower member of the pair. If it is, then both levels are rapidly ionised at similar temperatures and the electron and hole move rapidly through the crystal, only to be retrapped at pairs with a much larger separation $r$. This will then promote the luminescence from more widely separated pairs with lower transition energies and lead to an accompanied red-shift of the PL with an increase in temperature. In the event that the ionisation energy of the shallower level is still significantly smaller than that of the reduced level, the deeper level remains stable and the free carrier of the ionised defect may become re-trapped at neighbouring impurities and undergo recombination. This is most likely to occur amongst nearest neighbouring pairs thereby leading to a blue-shift of the line with respect to increasing temperature.

However, compensation may also explain the accompanied red shift of this line with increasing temperature. For low temperature measurements, electrons and holes are localised in any number of minima and maxima as a result of fluctuations in the band edges. Recombinations can only occur between electrons and holes localised on distant acceptors (termed tail impurity recombination). There is a thermal redistribution of carriers at higher temperatures, caused by the electrons and holes tunnelling (or surmounting the potential energy barrier) through to neighbouring minima and maxima. Electrons and holes will then relocalise in minima and maxima of a lower or higher energy and, hence, a red-shift will be measured. High levels of compensation is a well-known occurrence for the chalcopyrite materials (e.g. Bauknecht et al., 2000b; Yu et al., 1974), and this mechanism is considered the most likely cause for the observed red-shift with increasing temperature.
7.2.3 Low-energy photoluminescence

The low-energy PL (lines #3 and #4) occurring between ~2.3 and ~2.1 eV is often the most dominant line in all of the samples analysed in this study. The behaviour of these lines with respect to excitation intensity for the same samples described in the previous section (sample A and sample C) is illustrated in Fig. 7.22.

![Figure 7.22](image)

**Figure 7.22.** Excitation intensity dependence PL highlighting line #4 for Cu-rich material (a) and line #3 for slightly Ga-rich material (b). Temperature ~14 K.

For Cu-rich material, the position of line #4 undergoes a significant blue-shift with an increase in laser power over almost three orders of magnitude. This position of this line is depicted by the open squares in Fig. 7.23 (a) and blue-shift of ~21 meV/decade increase in laser power is measured. Line #3 in sample C follows a similar trend. The position of this line is represented by the solid squares in Fig. 7.23 (a) and also shows a large blue-shift with an increase in laser power (20 meV/decade). It is well known (Eberhardt et al., 2003) that relatively small blue-shifts with increasing laser power are
typical for $D^0A^0$ recombinations. However, this large blue-shift (over 60 meV) suggests the existence of potential fluctuations within the bands as a result of the random distribution of charged and unscreened defects in compensated semiconductors (Yu, 1977).

![Figure 7.23](image)

**Figure 7.23** The positions of lines #3 and #4 are plotted as a function of excitation intensity in (a). A double logarithmic plot of the integrated intensities of line #3 and #4 are displayed in Fig. 7.22 (a).

Fig. 7.23 (b) illustrates the intensity dependence of line #3 and #4 with respect to excitation intensity on a double logarithmic scale. The Cu-rich sample (A) is represented by the open squares, whereas the Ga-rich sample (C) is represented by the solid squares. Line #3 in sample C exhibits a superlinear dependence with excitation intensity ($k = 1.2$), whereas sample A depicts a linear relationship of line #4 ($k = 1.0$) with respect to excitation intensity. These values are arguably within experimental error.

The temperature dependence of the PL of the same samples illustrated in Fig. 7.22, is illustrated in Fig. 7.24. A strong red-shift in peak energy is observed with increasing temperature for both line #3 and line #4 for the Ga-rich and Cu-rich samples respectively. In the case of the slightly Ga-rich sample, line #3 appears to quench at relatively high temperatures (above 220 K) in favour of lower-energy luminescence. The peak positions are plotted as a function of temperature in Fig. 7.25 (a). For sample A, line #4 is centred at 2.107 eV and shifts by as much as 60 meV to a value of 2.047 eV at a temperature of 90 K. Higher temperature measurements were not recorded for this sample.
Figure 7.24  Temperature dependent PL highlighting the lower-energy region of the spectra for a Cu-rich layer (a) and slightly Ga-rich layer (b). Laser power ~5.4 mW.

Figure 7.25  The positions of line #3 and #4 are plotted as a function of temperature in (a). Arrhenius plot of the integrated intensities of these lines with respect to temperature (b).

Line #3 in sample C exhibited a total shift of over 264 meV between 14 K and room temperature at average shift of ~1 meV/K.
From the Arrhenius plot of integrated intensity versus temperature (Fig. 7.25 (b)), an activation energy of 55 meV can be calculated for line #3 using a straight line fit to the high temperature region.

Red PL (line #5) was observed in many of the Ga-rich samples that were analysed. Two entirely different samples to those previously discussed were chosen to describe the behaviour of this line. Sample D was analysed to be nearly stoichiometric (Cu/Ga ≈ 0.83), whereas sample E was significantly Ga-rich (Cu/Ga ≈ 0.70). The S/(Cu+Ga) ratios in the solid for each layer is within experimental error.

Figure 7.26. Excitation intensity dependence PL highlighting line #5 for a slightly Ga-rich layer (a) and a significantly Ga-rich layer (b).

The excitation dependence for both samples is represented in Fig. 7.26. Sample E, with the lowest Cu/Ga ratio in the solid, exhibits the strongest contribution from this line. The intensity of this line for both sample D and sample E has a linear dependence on excitation intensity as seen from Fig. 7.27 (a). Although a linear relationship is unusual
For a D⁰A⁰ transition, the possibility of a F-B transition can be excluded owing to the strong shift of this line to higher energies with an increase in laser power (see Fig. 7.27 (b)). For sample D (Cu/Ga = 0.83), a blueshift of ~29 meV/decade increase in laser power is observed (solid squares). This tendency is not quite as severe in sample E (Cu/Ga = 0.70) with a shift of ~13 meV/decade increase in laser power. In addition, this line is situated at a slightly lower overall energy for sample E than for sample D. This is ascribed to increased compensation in sample E. A high level of compensation also provides a plausible explanation for the large blue-shift observed for these lines with increasing laser power.

![Figure 7.27](a) Double logarithmic plot of the integrated intensities of line #5 for each of the series of spectra of the Ga-rich layers D and E depicted in Fig. 7.26. (b) Position of these lines plotted as a function of excitation intensity.

The influence of temperature on the PL of sample D and sample E is illustrated in Fig. 7.28. The position of this line red-shifts by a value of ~18 meV from 1.749 eV to 1.731 eV in the temperature range 10 K - 105 K (~0.19 meV/K). Sample E displays a similar trend and shows a red-shift of ~14 meV from 1.758 eV to 1.744 eV (~0.21 meV/K) with an increase in temperature. Thermal quenching of this band occurs above ~105 K (see sample E in Fig. 7.28 (b)). Fig. 7.29 illustrates the shift in the peak position for both sample D and sample E, with sample D exhibiting a larger shift than sample E. Over a temperature increase of ~100 K, sample D shifts from ~1.758 eV to 1.735 eV (33 meV), whereas sample E shifts from ~1.752 eV to 1.735 eV (17 meV).
Figure 7.28  Temperature dependent PL highlighting the behaviour of line #5 for sample D (a) and sample E (b). Laser power ~11 mW

Figure 7.29  The positions of the dominant line (#5) plotted as a function of temperature.
7.3 Summary

The PL obtained from the samples grown in this study can be sub-divided into three broad categories: near band-edge luminescence, green luminescence (~2.4 eV) and low-energy luminescence (2.25 eV - 1.8 eV). It was shown that the optical quality of grown epilayers is strongly dependent on the Cu/Ga ratio of the solid. Near-band edge luminescence, centred at ~2.48 eV (#1), was found for both Cu-rich and slightly Ga-rich epilayers. The position of this line was independent of excitation power and followed the band gap dependence with respect to temperature, suggesting that it is excitonic in nature. An activation energy of ~32 meV was calculated for the Cu-rich sample, which was the most resolved excitonic line in this work.

Green luminescence (line #2) was observed at ~2.32 eV for a Cu-rich sample and at ~2.38 eV for both a near-stoichiometric sample and slightly Ga-rich sample. This line exhibited a blue-shift with increasing laser power and was therefore attributed to a relatively shallow D\(^0\)A\(^0\) pair transition. The red-shift of this line with an increase in the measurement temperature is likely a result of compensation within the semiconductor. An activation energy of ~27 meV was calculated for this line in the slightly Ga-rich material.

The low-energy PL in the yellow spectral region was often the most dominant line in all of the samples analysed in this study. A line centred at ~2.25 eV (#3) was typical for near-stoichiometric to slightly Ga-rich material, whereas a different line centred at ~2.1 eV (#4) was typical for Cu-rich material. Both lines (attributed to different D\(^0\)A\(^0\) pair recombinations) exhibited a blue-shift with increasing excitation power and a large red-shift with increasing temperature. The line typical for Ga-rich material exhibited a red-shift (and an accompanied line broadening) with a decrease in Cu/Ga ratio in the solid. Similarly, the line typical for Cu-rich material also exhibited a red-shift and line broadening with an increase in the Cu/Ga ratio of the solid. These trends were attributed to a high degree of compensation for both Ga-rich and Cu-rich material. An activation energy of the order of ~55 meV was calculated for the line typical for Ga-rich material.
Red PL at ~1.8 eV (line #5) dominated for material with a significantly Ga-rich composition. A significant blue-shift with increasing laser power implied that this transition was also $D^0A^0$ in nature. The red-shift in this line with decreasing Cu/Ga ratio in the solid and the red-shift with increasing temperature also suggested a high degree of compensation.

From the results presented in this chapter, the nature of the intrinsic defects responsible for the photoluminescence observed can be speculated upon. According to Zhang et al. (1998) the defect formation energies for CuInSe$_2$ vary with respect to changes in the electronic potential (i.e. the position of the Fermi level) and with the chemical potential of the atomic species (i.e. changes in the composition of the solid). For slightly In-rich and Cu-poor material, the order of formation energies (excluding the $V_{Se}$) were: $V_{Cu} < In_{Cu} < V_{In} < Cu_{In} < Cu_i$ for $p$-type material. In that study the most dominant defects for In-rich, Cu-poor material (similar to the Ga-rich, Cu-poor nature of most samples described in this present study), were the $V_{Cu}$, $V_{In}$ and $In_{Cu}$. For Cu-rich, In-poor material, the dominant defects were the $Cu_{In}$, $V_{Cu}$ and $V_{In}$. Assuming a similar order for defect formation energies in CuGaS$_2$, the most likely defects for the material described in the present work are the $V_{Cu}$, $V_{Ga}$, $Ga_{Cu}$ and $Cu_{Ga}$. The $V_S$ is considered to be a relatively shallow donor in many studies (Metzner et al., 2004; Botha et al., 2001; Shirakata and Chichibu, 2000) and cannot be ignored.

In the present study, the three dominant lines occurring at ~2.4 eV, ~2.25 eV (for Ga-rich material) and ~2.1 eV (for Cu-rich material) were attributed to $D^0A^0$ pair recombination. One can expect the $V_{Cu}$ formation energy to also be comparatively low in CuGaS$_2$ and one would expect this defect to be present in significant densities for near-stoichiometric and slightly Ga-rich material. This is supported by Bellabarba et al. (1996) who found evidence that the dominating acceptor level in near stoichiometric to slightly Ga-rich material is the $V_{Cu}$. Since the line labeled #2 in this chapter (~2.4 eV) is observed in layers exhibiting a similar composition, the acceptor level of this pair is tentatively assigned to the $V_{Cu}$. The $V_S$ is considered to be the shallowest of all donor levels.
(Metzner et al., 2004; Botha et al., 2001; Shirakata and Chichibu, 2000), and therefore we tentatively assign the donor level of this defect pair to the $V_S$.

Increasingly Ga-rich layers are likely to have high levels of the Ga$_{Cu}$ antisite (a donor) in addition to the $V_{Cu}$. The line centred at ~2.25 eV (#3) is observed for slightly Ga-rich material and as such this line is tentatively ascribed to emissions involving the $V_{Cu}$ and Ga$_{Cu}$ antisite. Cu-rich material is often characterised as S-poor and as such the $V_S$ and Cu$_{Ga}$ antisite is tentatively assigned to the donor and acceptor levels, respectively, giving rise to the line centred at ~2.1 eV (#4). The deep PL measured at ~1.8 eV is most often observed for significantly Ga- and S-rich material. It is therefore plausible that this line involves the Si, in association with an unknown donor.

Metzner et al. (2004) speculated that a shallow donor (attributed to the $V_S$) and the $V_{Cu}$ and $V_{Ga}$ contribute to two $D^0A^0$ transitions found at 2.410 eV and 2.390 eV. Honda et al. (1993) described a $D^0A^0$ pair recombination at 2.42 eV, whereas Shirakata and Chichibu (2000) described a similar recombination at 2.40 eV between an acceptor level at 100 meV and a donor level at 46 meV, ascribed to the $V_{Cu}$ and $V_S$ respectively. This assignment is similar to that of Miyazaki et al. (1991) for the 2.4 eV line observed in bulk CuGaS$_2$ crystals. From these studies a better understanding emerges of the radiative mechanisms dominating for Cu-rich and Ga-rich layers. Due to the broad nature of the lines observed in this study, it was not possible to calculate the defect levels associated with the likely defects outlined above.
CHAPTER 8

CONCLUDING REMARKS

In this study, the MOVPE growth and characterisation of the CuGaS$_2$ chalcopyrite is described. The purpose of this work is to gain a better understanding of the nature of intrinsic defects common to this class of semiconductors by relating the optical and structural properties to the composition of the layers studied.

Layers grown in this study exhibited non-uniformities in the composition and surface morphology, both laterally and in the direction of the carrier gas flow. A decrease in the Cu/Ga ratio of the solid in the direction of the carrier gas flow suggested Cu was the limiting species at the growth interface. A series of layers grown with changing VI/(I+III) ratios in the vapour phase indicated a possible pre-reaction between the Cu and S metalorganics. This is likely a contributing factor to Cu being the limiting species. In addition to this complication, the vapour pressure of Cu(hfac)$_2$⋅Et$_3$N was found to decrease with repeated use over time owing to a loss of the volatile ligand Et$_3$N. Latter layers (which form the bulk of this study) were grown once the vapour pressure had stabilised to that of the reduced molecule Cu(hfac)$_3$.

In this study, the stoichiometric composition of CuGaS$_2$ was found to occur for a measured Cu/Ga ratio of ~0.84, which was attributed to the EDS analysis used. Cu-rich material typically exhibited a rough surface morphology, whereas Ga-rich material was characteristically smoother. In some cases, the compositional non-uniformity was used to good effect by comparing the structural and optical properties for various regions within individual samples. For one such example, Cu-rich regions at the leading edge of a sample grown on GaAs typically exhibited polycrystalline growth, whereas the Ga-rich regions at the trailing edge typically exhibited c-axis orientated epitaxial growth. This trend was observed for a number of samples of varying compositions. In extreme cases of non-stoichiometry, the Cu$_x$S$_y$ and Ga$_x$S$_y$ binary phases were identified by XRD, and the presence of Ga$_2$S$_3$ was confirmed by Raman spectroscopy.
A Cu-rich sample grown on a Si substrate was analysed by RBS for the purpose of comparing the measured composition with that obtained from the more commonly used method (i.e. EDS). Due to a large peak overlap between the Cu and Ga contributions in the RBS spectra, and the rough surface morphology, considerable inconsistencies were found in the Cu/Ga ratio as determined by each technique. However, the S/(Cu+Ga) ratios determined by each technique were comparable. In order to accurately simulate the RBS spectra, it was necessary to describe the sample in terms of a smoother, underlying layer and rougher surface layer (a property confirmed by cross-sectional TEM analysis).

The effect of changing growth parameters on the structural and optical properties of the material was also investigated. An increase in the substrate temperature from 550°C to 600 °C resulted in the formation of Cu-rich crystallites on the layer surface and a severe loss in the optical quality of the material. High resolution TEM indicated that substrates exhibited severe degradation at the substrate/layer interface when the Ga dangling bonds of the GaAs substrate were not S-terminated prior to growth. Substrates undergoing this treatment exhibited a significant improvement in the epitaxial quality. A decrease in the concentration of the reagents in the vapour phase resulted in the polycrystalline growth of CuGaS$_2$ as opposed to $c$-axis orientated epitaxial growth. This change, however, had no apparent effect on the optical quality of the thin film.

The exact structural nature of the CuGaS$_2$ phase was difficult to determine by XRD alone, and conventional TEM analysis of a near-stoichiometric layer illustrated the epitaxial growth of the disordered zincblende and CuPt structure types. In addition to these polytypes, the chalcopyrite phase was identified (by XRD) as the randomly orientated crystallites present on the surface of this epilayer. In addition to the simultaneous growth of several polytypes of CuGaS$_2$ within a single sample, the possible formation of an ordered defect compound was also discussed. A careful study by XRD relating the position of the 004 line to that of the Cu/Ga ratio in the solid illustrated significant broadening of this line in addition to a shift to higher $2\theta$ values for samples with a significantly low Cu/Ga ratio in the solid. This shift was attributed to the formation of the ordered defect compound, CuGa$_3$S$_5$ for increasingly Ga-rich material.
The PL obtained from the samples grown in this study could be sub-divided into three broad categories: near band-edge luminescence, green luminescence (~2.4 eV) and low-energy luminescence (2.25 eV - 1.8 eV). By comparing the PL response across a single epilayer of a known composition, a better understanding of the effect of composition on the optical quality could be obtained. From these measurements it was shown that the PL of grown epilayers is strongly dependent on the Cu/Ga ratio of the solid. A defect scheme was suggested, which accounted for the changes in the composition of the layers analysed.

Unresolved excitonic luminescence was found for both Cu-rich and slightly Ga-rich samples. A line at ~2.4 eV was attributed to recombinations between the $V_S$ and $V_{Cu}$, $D^0 A^0$ pair and was found for near-stoichiometric samples only. Separate lines for Ga-rich and Cu-rich material were observed at ~2.25 eV and 2.1 eV, respectively. These $D^0 A^0$ pair recombinations were speculated to involved the $V_{Cu}$ and $Ga_{Cu}$, and $V_S$ and $Cu_{Ga}$, respectively. Red PL (~1.8 eV) dominated for material with a significantly Ga-rich composition. The $Si$ was the suggested acceptor in this $D^0 A^0$ pair recombination.

Owing to the exaggerated blue-shift of the low-energy luminescence with increasing laser power, and the red-shift with increasing temperature, all layers were considered highly compensated. The large changes in composition across the epilayer surfaces are a likely cause for the high degree of compensation observed.
APPENDIX

Publications by this author in peer-reviewed journals

2005  MS Branch, PR Berndt, AWR Leitch, JR Botha, J Weber

2004  MS Branch, PR Berndt, AWR Leitch, JR Botha, J Weber

               MS Branch, PR Berndt, AWR Leitch, J Weber, JR Botha

2003  MS Branch, PR Berndt, JR Botha, AWR Leitch, J Weber

Contributions by this author at international conferences

2005  MS Branch, PR Berndt, AWR Leitch, JR Botha, J Weber
“The influence of growth parameters on the structure and composition of CuGaS$_2$ epilayers grown by MOVPE”

2004  MS Branch, PR Berndt, AWR Leitch, JR Botha, J Weber
“An investigation into the influence of various metalorganic sources on the quality of MOVPE-grown CuGaS$_2$”

2002  MS Branch, PR Berndt, JR Botha, AWR Leitch, J Weber
“Structure and morphology of CuGaS$_2$ thin films”
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