5.1 Introduction

The optimization of the structural properties (surface morphology, adhesion and composition uniformity) of the chalcopyrite absorber films is an important prerequisite for successful fabrication of high efficiency solar cells. In this study, a variety of ternary and quaternary absorber films were deposited with a classical two-step growth process (i.e. selenization and/or sulfurization of vacuum deposited precursors). As a point of reference, device quality CuInSe$_2$ thin films were deposited via the reactive annealing of selenium-containing precursors (e.g. InSe/Cu/InSe stacks) in elemental Se vapour under sub-atmospheric conditions. This technique produced large-grained, single phase CuInSe$_2$ thin films with a high degree of in-depth composition uniformity.

In an attempt to increase the band gap of the thin films, CuIn(Se,S)$_2$ thin films were prepared by thermal diffusion of sulfur into CuInSe$_2$. This post-sulfurization process, however, had limited success and resulting films were heterogeneous. In a second attempt to modify the band gap of the alloys, Cu(In$_{1-x}$Ga$_x$)Se$_2$ films were prepared. In this case, sequentially evaporated gallium-containing precursors (e.g. GaSe/InSe/Cu stacks) were reacted to elemental Se vapour. The deposition sequence during the precursor formation step, the GaSe deposition temperature, the selenization temperature, as well as the concentration of gallium in the alloys were systematically varied in order to optimize the material quality of Cu(In$_{1-x}$Ga$_x$)Se$_2$ thin films. These studies were successful and single-phase quaternary alloys were prepared under
optimum experimental conditions. Optimum absorber structures were finally used to produce completed solar cell devices. The most important results that followed from the respective studies will be discussed in this chapter.

5.2 Deposition of CuInSe$_2$ Absorber Films

5.2.1 Introduction

In typical two-step growth processes, copper-indium metallic alloys are reacted to elemental Se vapour or a H$_2$Se/Ar gas mixture. This normally results in CuInSe$_2$ absorber films with poor structural properties (i.e. non-uniform surface morphologies with segregated CuSe binary phases). In order to prevent these growth related problems, pure metallic In was replaced by InSe during the deposition process. The inclusion of Se into the precursor structure resulted in absorber films with improved morphological features and compositional homogeneity. The order of deposition of the precursor layers (i.e. Cu/InSe, InSe/Cu and InSe/Cu/InSe) was also varied in order to optimize the structural features of the precursors films. These films were simultaneously selenized in elemental selenium vapour, under the experimental conditions described in Section 4.4.3.2.

5.2.2 Structural features of Cu-In-Se precursors

Precursors refer to the crystalline state of the thermally deposited films prior to reaction to selenium vapour at temperatures around 550ºC. The various precursors were deposited under identical vacuum conditions onto the Mo films at 200ºC. The Mo was prepared under the optimized conditions described in Section 4.3. It is therefore reasonable to assume that the underlying Mo layer had very little influence on the
morphology of the final alloys. Three types of precursor structures were prepared: (i) an In$_x$Se$_y$ layer over a Cu layer (ii) a Cu layer over an In$_x$Se$_y$ film and (iii) triple layers comprising InSe/Cu/InSe. It is well known that the final surface morphology of a specific chalcopyrite alloy is significantly influenced by the overall bulk composition of the film. In order to maintain comparable compositional ratios, the total layer thicknesses of the In$_x$Se$_y$ and the Cu layers were kept constant at 1.5 µm and 0.2 µm, irrespective of the order of deposition.

It is important to mention that Mo, Cu as well as InSe deposited as extremely smooth films on the glass substrates. However, the respective precursor structures on glass/Mo exhibited morphological structures which greatly depended on the sequence of deposition.
Figure 5.1: SEM micrographs demonstrating the structural features of (a) Mo/Cu/InSe, (b) Mo/InSe/Cu and (c) Mo/InSe/Cu/InSe precursors deposited at 200°C on glass/Mo substrates.
In the case of Mo/Cu/InSe structures, SEM studies (Fig. 5.1(a)) revealed a non-uniform surface morphology with irregular shaped grains superimposed on smooth flat background material. EDS analysis revealed that the large, irregular structures were In-rich. SEM studies (Fig. 5.1(b)) revealed a more dense structure consisting of large elongated grains (>0.5 µm) when the InSe layers were first deposited onto the Mo substrates, followed by Cu deposition. Figure 5.1(c) is a SEM micrograph of a typical triple layer, InSe/Cu/InSe, deposited onto a glass/Mo substrate at 200°C. In this case, the precursor morphology was dominated by the presence of a high density of mostly spherical grains with typical grain sizes between 0.5 and 1 µm. These results indicated that the degree of alloying between the precursor elements depended on the deposition sequence and improved when the Cu layer was sandwiched between InSe layers.

The corresponding XRD patterns from the respective precursor films are depicted in Fig. 5.2.

![XRD pattern](image)
Figure 5.2: X-ray diffraction spectra of the (a) Cu/InSe (b) InSe/Cu and (c) InSe/Cu/InSe precursors deposited on Mo/glass at a substrate temperature of 200°C. The XRD spectra were measured with a Co source (\(\lambda = 1.7890\) Å).
The presence of the characteristic (112) diffraction peak of the chalcopyrite lattice, irrespective of the order of deposition, is indicative of the partial formation of CuInSe$_2$ due to an interdiffusion between Cu-selenide and In-selenide binary phases. The remaining peaks are due to diffraction from the remaining binary phases (e.g. CuSe$_2$, CuSe and InSe) in the partially reacted alloys. It is also important to note that the volume fraction of binary phases significantly reduced in the case of InSe/Cu/InSe precursor structures (see Fig. 5.2 (c)). This phenomenon is related to an improved alloying between the individual layers in the precursor stack in accordance with the SEM observations in Figure 5.1.

5.2.3 Structural features of CuInSe$_2$ thin films.

The ultimate aim of this part of the study was to deposit uniform and large-grained CuInSe$_2$ absorber films. Based on the results discussed in the previous section, InSe/Cu/InSe films were selected as precursor structures. These precursors were subsequently reacted in vacuum to elemental Se vapour at 550°C for 60 minutes, according to the procedure outlined in Section 4.4.3.2.

Figure 5.3 (a) is a SEM micrograph of the typical surface morphology of a CuInSe$_2$ thin film, produced by the above referred to procedure. The reaction of the InSe/Cu/InSe precursor to elemental Se vapor at 550°C for 60 minutes produced uniform, large grained (> 1µm) films with a tightly packed structure. XRF K$_{\alpha1,2}$ measurements indicated that the bulk composition of this specific film was 23.31 at.% Cu, 25.89 at.% In and 50.8 at.% Se. Figure 5.3(b) is a XRD pattern from the CuInSe$_2$ film shown in Fig. 5.3 (a). The superior structural properties of the CuInSe$_2$ thin film are clearly reflected by the XRD results in Fig. 5.3(b).
Figure 5.3 (a): Representative surface morphology of a CuInSe$_2$ thin film produced by the reaction of a glass/Mo/InSe/Cu/InSe precursor to elemental Se vapour at 550 °C for 60 minutes.

Figure 5.3 (b): XRD patterns for CuInSe$_2$ films shown in Fig 5.3 (a), measured by Cu K$_\alpha$ radiation (1.5418 Å).
In general, the XRD from these films were characterized by the presence of sharp, well-defined chalcopyrite peaks with no evidence of secondary phases. In addition, these films exhibited a strong preferred (112) orientation. The preferred (112) orientation of the films is in accordance with the observed columnar grain structure of the CuInSe$_2$ layers (see Fig. 5.3 (a)).

5.2.4 In-depth compositional uniformity of selenized films

The in-depth compositional uniformity of the final CuInSe$_2$ thin films were estimated by etching the samples repeatedly in bromine methanol, followed by measurements of the characteristic XRF K$_{\alpha1,2}$ line intensities of the remaining material after each etching step. A detailed discussion of this procedure was presented in Section 4.6.2.4.

![Figure 5.4: In-depth compositional uniformity of the CuInSe$_2$, shown in Fig. 5.3(a). The etching profile was produced by measuring the XRF K$_{\alpha1,2}$ line intensities of the remaining material after 5 successive etching steps in Br$_2$/MeOH.](image)

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<table>
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<tr>
<th>Etching Step</th>
<th>Film Mass (mg cm$^{-2}$)</th>
<th>Element concentration (at%)</th>
<th>Atomic Ratio</th>
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<td></td>
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</tr>
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<td>25.78</td>
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<tr>
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</tr>
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<tr>
<td>5</td>
<td>0.45</td>
<td>23.48</td>
<td>25.14</td>
</tr>
</tbody>
</table>

Table 5.1 Summary of the in-depth XRF data presented in Fig 5.4, obtained from a repeatedly etched CuInSe$_2$ sample in bromine methanol. Etching step 0 represents the compositional properties of the unetched sample.

The element concentrations as function of material mass per area (mg/cm$^2$) are depicted in Figure 5.4 for a typical CuInSe$_2$ sample prepared by the reaction of an InSe/Cu/InSe precursor to elemental Se vapour. It should be realized that these etching profiles represent the compositional features of the material remaining after successive etching steps. The compositional properties of the unetched sample and that of the remaining material after each etching step are also summarized in Table 5.1. It is
important to note that the Cu/In atomic ratio and Se concentration of the CuInSe$_2$ films (see Fig. 5.4) remained remarkably constant throughout the depth of the film. It is also important to point out that this etching profile represents the general in-depth compositional properties of the CuInSe$_2$ films produced during this study.

5.3 Preparation of CuIn(Se,S)$_2$ Thin Films

5.3.1 Introduction

In an attempt to increase the band gap of the absorber layers, the ternary alloys were subsequently sulfurized. The systematic replacement of Se with smaller S atoms results in a shrinkage of the chalcopyrite lattice and ultimately in an increase in band gap. An increase in band gap in turn results in an increase in the open-circuit voltage of photovoltaic devices.

5.3.2 Structural features of the CuIn(S,Se)$_2$ thin films

The optimized CuInSe$_2$ thin films, discussed in the previous section, were used as reference samples for the sulfurization experiments. The experimental procedure followed during the solid-state diffusion process was discussed in Section 4.4.3.3. Experimentally it was found that the sulfurization period, reaction temperature and position of the sulfur with respect to the samples critically influenced the degree of sulfur incorporation into the CuInSe$_2$ absorber films. Also, in the total absence of additional Se during the sulfurization process, the CuInSe$_2$ films were rapidly depleted of Se resulting in the formation of single-phase CuInS$_2$. The rapid loss of Se from the thermally treated CuInSe$_2$ samples at temperatures at or above 200°C has been reported elsewhere [Klenk et al., 2001]. The selenium pellets were placed in close contact to the reference
CuInSe₂ samples, while the sulfur was positioned at least 20 cm away from the samples in the direction from where the Ar entered the tube. This lateral displacement of the chalcogen solid sources was essential in order to counter the rapid out-diffusion of Se from the samples and hence achieve a systematic and controlled substitution of Se species with S at the absorber surface. Figure 5.5 (a) represents the typical surface morphology of a CuInSe₂ film, sulfurized at 500°C for only 15 minutes, under the experimental conditions described above.

![SEM micrograph](image)

Figure 5.5 (a): SEM micrograph depicting the typical surface morphology of a CuIn(Se,S)₂ thin film. This film was obtained by the solid-state diffusion of S into CuInSe₂ at 550°C for 15 minutes.

XRF analysis revealed that the bulk composition of the sulfurized sample was 20.92 at.% Cu, 23.41 at.% In, 45.38 at.% Se and 10.29 at.% S. Under these specific experimental conditions only minor changes in the structural features (i.e. the average grain sizes and shapes) of the films were observed. Comparison of this specific sulfurized absorber film (Fig 5.5 (a)) with the untreated CuInSe₂ reference sample (Fig.
5.3(a)), revealed the presence of small crystallites superimposed on the large-grained background material. The presence of these crystallites after sulfurization resulted in a marginal increase in the surface roughness of the film. The XRD pattern (see Fig. 5.5(b)) of the sulfurized sample revealed an asymmetrical broadening of [112], [220/204] and [312/116] diffraction peaks as a result of the sulfur incorporation into the CuInSe₂ structure.

![XRD pattern](image)

Figure 5.5 (b): XRD pattern for CuIn(Se,S)₂ film shown in Figure 5.5 (a), measured with Cu Kα radiation (1.5418Å).

It is also interesting to note that the position of the [112] diffraction peak at about 26.85° is at a significantly higher 2θ-value than the expected value for the pure CuInSe₂ phase (see Fig. 5.3(b)). This increase in the 2θ-value, which corresponds to a decrease in lattice parameter, is indicative of an incorporation of S in the near-surface region of the CuInSe₂ absorber layer. The shoulders to the right of the characteristic peaks are due to increasing amounts of S towards the Mo back contact region, which resulted in a
shrinkage of the chalcopyrite lattice and hence the observed continuous increase in the 2θ-value of the diffraction peaks. It is also important to mention that for higher sulfur concentrations in the absorber films (i.e. above 20 at. %), XRD studies revealed a dramatic deterioration in crystalline quality. This was normally reflected by a substantial reduction in peak intensity, increase in the full-width at half maximum (FWHM) values of the diffraction peaks as well as the presence of separated CuInSe$_2$ and CuInS$_2$ phases.

### 5.3.3 In-depth compositional uniformity of sulfurized films

The in-depth compositional features of the sulfurized samples were determined by XRF studies, as outlined in Section 4.6.2.4. The element concentrations as function of material mass per area (mg/cm$^2$) are depicted in Figure 5.6 for a typical CuIn(Se,S)$_2$ sample prepared during this study.

![Figure 5.6: In-depth compositional uniformity of the CuIn(Se,S)$_2$ sample shown in figure 5.5 (a) The etching profile was produced by measuring the XRF K$_{α1,2}$ line intensities of the remaining material after 5 successive etching step in Br$_2$/MeOH.](image)

Figure 5.6: In-depth compositional uniformity of the CuIn(Se,S)$_2$ sample shown in figure 5.5 (a) The etching profile was produced by measuring the XRF K$_{α1,2}$ line intensities of the remaining material after 5 successive etching step in Br$_2$/MeOH.
Table 5.2: Summary of the XRF data presented in Figure 5.6. Etching step 0 represents the bulk compositional properties of the unetched sample.

The compositional properties of the unetched sample and that of the remaining material after each etching step is also summarized in Table 5.2. Interesting changes in the compositional depth profile were observed after sulfurization. It is clearly evident from Figure 5.6 that the Cu/In atomic ratio remained relatively constant through the depth of the film, while the sulfur and selenium concentrations varied significantly with sample depth. In this regard, it is important to note that a higher concentration of sulfur was detected at the top surface and back-contact regions than in the interior part of the film, which confirmed the XRD results in Figure 5.5 (b). These results therefore indicated that
band gap grading of these polycrystalline semiconductor thin films are possible by the
controlled solid-state diffusion of sulfur into CuInSe$_2$.

5.4 Formation of Cu(In,Ga)Se$_2$ Thin Films

5.4.1 Introduction

Another promising method to increase the band gap of CuInSe$_2$ is by the systematic
replacement of In with smaller group III atoms such as Ga or Al. This results in a
decrease in the lattice parameters of the chalcopyrite lattice and ultimately in an
increase in band gap. In classical two-step growth processes, Cu-In-Ga metallic
precursors are selenized in elemental Se vapour or a H$_2$Se/Ar gas mixture to form
Cu(In,Ga)Se$_2$. A seemingly insurmountable disadvantage of these processes is that the
resultant semiconductor absorber films are heterogeneous. Due to the difference in the
reaction rates between the binary selenides, the bulk of the material contains discrete
CuInSe$_2$ and CuGaSe$_2$ phases [Marudachalam et al., 1997]. Alternatively, graded film
structures are obtained with most of the gallium located at the back of the film. This
implies that the gallium does not increase the band gap of the absorber in the active
region of the solar cell, and complete devices are therefore limited to relatively low
open-circuit voltages.

In order to investigate and ultimately to solve these reported growth-related problems,
the following experimental conditions were investigated:

- Selenium-containing Cu-In-Ga-Se precursors were used compared to the metallic
  Cu-In-Ga films used in standard two-step growth processes.
- Six different precursor structures were investigated in order to modify the diffusion
  behaviour of gallium in the final compound semiconductor films.
• The selenization conditions in elemental Se vapour were carefully investigated in order to understand especially the influence of the reaction temperature on the material quality of the quaternary alloys.

• It was also anticipated that the GaSe deposition temperature during the precursor formation step could critically influence the degree of alloying with InSe and Cu. This phenomenon was investigated by maintaining the deposition temperature of the InSe and Cu layers constant at 200°C, while that of GaSe was varied between 200°C and 400°C.

• The concentration of gallium in the quaternary alloys were altered by variation in the relative thickness of GaSe with respect to InSe and Cu during the formation of the precursors. The gallium concentration in the Cu(In,Ga)Se₂ films was measured with XRF, and the shift in lattice parameters (measured with XRD) were compared with the predicted theoretical values from Vegard’s law for single-phase material.

From these systematic studies it was possible to predict optimum growth conditions for the deposition of single-phase Cu(In,Ga)Se₂ with a modified band gap. The most important results that followed from the individual studies are highlighted in the following sections.

5.4.2 Influence of the stacking order on structural features of the Cu-In-Ga-Se precursors

Figures 5.7 (a) to (f) depict SEM micrographs of the surface morphologies of sequentially deposited Cu-In-Ga-Se precursor films on molybdenum coated soda lime glass substrate. The respective layers in the precursor structures were deposited at
200°C, under the conditions described in Section 4.4.3.1. Irrespective of the order of deposition, the thicknesses of the respective layers in the stack (200 nm Cu, 200 nm GaSe and 1500 nm InSe) were maintained constant. Fig. 5.7 (a) represents the typical morphological features of a Mo/Cu/InSe/GaSe precursor film. These films were relatively dense and consisted of large (0.5 –1 µm) spherical grains, but exhibited poor adhesion properties. The Mo/InSe/Cu/GaSe precursor structures (see Fig. 5.7 (b)) were also dominated by the presence of a high density of mostly rounded grains with typical sizes between 0.2-0.8 µm. However, in these cases the films adhere well to the Mo/glass substrates. Fig. 5.7 (c) is a representative SEM micrograph of a typical Mo/GaSe/Cu/InSe precursor. A comparison between this micrograph and the previous micrographs clearly revealed a significant increase in the average grain size of the film when the GaSe was deposited directly onto Mo. Typically these films had grain sizes between 2 and 3 µm. The Mo/Cu/GaSe/InSe structures (Fig. 5.7 (d)) had a weakly defined grain structure with a “cauliflower” appearance. Figure 5.7 (e) is a SEM micrograph of a typical Mo/InSe/GaSe/Cu precursor, in which the GaSe layer was sandwiched between the InSe and Cu layers. Visually these films were extremely smooth and SEM studies revealed a layered structure. These specific structural features were retained in the case of Mo/GaSe/InSe/Cu precursors (Fig. 5.7 (f)). However, detailed SEM analysis revealed the presence of worm-like features superimposed on the smooth densely packed plate-like background material. Compositional analysis indicated that these worm-like structures were more Cu-rich compared to the background material.
Fig. 5.7: Surface morphologies of sequentially deposited (a) Cu/InSe/GaSe (b) InSe/Cu/GaSe (c) GaSe/Cu/InSe (d) Cu/GaSe/InSe (e) InSe/GaSe/Cu and (f) GaSe/InSe/Cu precursors onto Mo/glass substrates. These films were deposited at a substrate temperature close to 200°C.
The typical crystalline features of a gallium-containing precursor, deposited at 200°C onto Mo-coated glass substrates, are depicted in Figure 5.8. The partial formation of CuInSe$_2$ was reflected by the presence of the characteristic [112] diffraction peak of the chalcopyrite lattice at 26.75°. The expected binary phases (i.e. CuSe, InSe and GaSe) were also clearly visible in the depicted XRD spectrum, which confirmed the fact that the inter-diffusion process between the individual layers in the precursor stack was incomplete at this stage of processing. It is also important to mention that the order of deposition of the layers in the precursor stack had marginal influences on the crystalline quality of the precursor films. The relative intensities of the binary phases were for obvious reasons influenced by the order of deposition, but the specific binary phases shown in Figure 5.8 were detected in all the films.

![X-ray diffraction spectrum](image)

**Figure 5.8:** X-ray diffraction spectrum of a typical sequentially deposited Cu-In-Ga-Se precursor structure on Mo/glass at 200°C. The XRD spectrum was measured with Cu Kα radiation (1.5418 Å).
5.4.3 Relationship between precursor structure and material properties of the CuIn$_{1-x}$Ga$_x$Se$_2$ thin films

The precursor structures, discussed in the previous section, were subsequently exposed to elemental Se vapour in vacuum. It is important to mention that the thicknesses of the individual layers in the precursor stacks (200 nm Cu, 200 nm GaSe and 1500 nm InSe) were kept constant and that all these layers were deposited at a substrate temperature of 200°C. Assuming a homogeneous quaternary alloy, these thickness values should translate in absorber films with Cu/(In+Ga)- and Ga/(In+Ga)-atomic ratios of 0.85 and 0.25 respectively.

It is also important to realize that the selenization temperature critically influence the formation kinetics of the chalcopyrite absorber films. For the purpose of comparison, the precursors were therefore selenized under identical experimental conditions in elemental Se vapour, as outlined in Section 4.4.3.2. In order to ensure complete reaction, selenization studies were conducted at a temperature close to 550°C for 60 minutes. Selenization of the Mo/InSe/GaSe/Cu and Mo/GaSe/InSe/Cu structures (see Figs. 5.7 (e) and (f)) resulted in CuIn$_{1-x}$Ga$_x$Se$_2$ films with poor structural features (i.e. non-uniform morphologies and/or adhesion failure). As a result, these specific films were not considered during further investigations. Figures 5.9 (a) to (d) depict the typical morphological features of Cu(In,Ga)Se$_2$ films, produced after the precursors in Figs. 5.7 (a) to (d) were reacted to elemental Se vapour under the experimental conditions discussed above. Comparison of these SEM micrographs clearly revealed that the surface morphologies and hence surface roughness of the resulting Cu(In,Ga)Se$_2$ absorber films were significantly influenced by the structure of the precursor films prior to selenization. In this regard, it is important to keep in mind that
the structural features of the absorber films directly influence the conversion efficiencies of photovoltaic devices. In general, smooth and uniform absorber films are required to optimize the absorber/CdS/ZnO heterojunction properties [Tuttle et al., 1996]. The structural features of the selenized Mo/Cu/InSe/GaSe precursors (see Fig. 5.9(a)) were dominated by the presence of nodular grain structures with typical sizes between 0.5 and 1 μm. An exchange of the Cu and InSe layers in the precursor stack (i.e. Mo/InSe/Cu/GaSe) resulted in Cu(In,Ga)Se$_2$ absorber films with improved structural properties. As indicated in Figure 5.9 (b), these films were characterized by the presence of densely packed columnar grain structures with average grain sizes around 1 μm. In cases where growth was initiated with a GaSe layer and terminated with a InSe layer (see Fig. 5.9 (c)), Cu(In,Ga)Se$_2$ films exhibited large smooth faced crystallites with typical sizes between 2 and 5 μm. This large variation in grain size implied that these specific films were non-uniform with a relatively high level of surface roughness. Figure 5.9 (d) is SEM micrograph of a quaternary alloy which resulted after a Cu/GaSe/InSe precursor was annealed in elemental Se vapour at 550°C for 60 minutes. This stacking order resulted in a dramatic reduction in the average grain size of the chalcopyrite alloy with typical grain size well below 1 μm. As a result these films were dense and smooth compared to the other structures. However, the high density of sub-micron grains corresponds to a significant increase in the grain boundary density in the thin film. This in turn may result in deterioration in the electrical behavior of the solar cell device.
Figure 5.9: Surface morphologies of Cu(In,Ga)Se$_2$ thin films, produced by selenization of (a) Cu/InSe/GaSe (b) InSe/Cu/GaSe (c) GaSe/Cu/InSe (d) Cu/GaSe/InSe precursor structures under identical experimental conditions in elemental Se vapour at 550°C for 60 minutes.
Figure 5.10: Representative XRD pattern from the Cu(In,Ga)Se$_2$ films shown in Fig. 5.9. The respective precursor structures were deposited at 200°C on glass/Mo, followed by reaction to elemental Se vapour at 550°C for 60 minutes. The XRD spectrum was measured with Cu Kα radiation (1.5418 Å).

Figure 5.10 is a representative XRD patterns from the Cu(In,Ga)Se$_2$ samples shown in Figure 5.9. Irrespective of the stacking order during the precursor formation step, XRD analyses revealed the presence of a graded CuIn$_{1-x}$Ga$_x$Se structure. This phenomenon is represented by the asymmetric broadening of the characteristic [112], [220/204] and [312/116] diffraction peaks. In this regard, it is important to note that the position of the [112] diffraction peak close to 26.65° represents the lattice parameter of pure CuInSe$_2$, while the tail due to increasing amounts of gallium extends all the way to the peak position of CuGaSe$_2$. It is therefore reasonable to assume that the surface of the
absorber film contains pure CuInSe$_2$ and that the gallium increases continuously towards the Mo back contact. These observations are in good agreement with other related studies and are attributed to the difference in the formation kinetics of the two ternary phases [Marudachalam et al., 1997].

5.4.4 Influence of selenization temperature on crystalline quality of absorbers

In order to study the influence of the selenization temperature on the material quality of the absorbers, InSe/Cu/GaSe precursors were once again deposited onto glass/Mo at 200°C. The structural features of this specific precursor structure are depicted in Fig. 5.7 (b). The precursors were subsequently exposed to elemental Se vapour in vacuum under the experimental conditions outlined in Section 4.4.3.2. The substrate temperature during selenization was varied between 300°C and 600°C in order to modify the reaction kinetics of the process. The reaction period was maintained at 60 minutes in all cases and the temperature was ramped in ten minutes to the specific reaction temperature. Figures 5.11 (a) to (d) are SEM micrographs demonstrating the crystalline quality of the films after the annealing step in Se vapour at (a) 300°C, 400°C, 500°C and 550°C. Comparison of these micrographs clearly reveals the dramatic influence of the reaction temperature on the formation kinetics of the Cu(In,Ga)Se$_2$ thin films. Films that were selenized at low temperatures close to 300°C appeared visually uniform and exhibited the characteristic grey-black color of chalcopyrite thin films. However, SEM studies (see Fig. 5.11 (a)) revealed a non-uniform morphology that was dominated by the presence of large (2-3 μm) faceted crystallites superimposed on a background of sub-micron circular grains. The background material represented the unreacted precursor structure and/or the partial formation of the ternary alloy, while the
larger grains were related to the formation of Cu-rich binary phases (e.g. CuSe, CuSe$_2$ or Cu$_{2-x}$Se). An increase in selenization temperature to 400°C produced films that were characterized by the presence of nodular grain structures with typical sizes around 1 µm (see Fig. 5.11 (b)). These almost featureless nodular structures were transformed into agglomerates with defined grain structure as the selenization temperature was increased to 500°C. Close examination revealed that the agglomerates consisted of numerous sub-micron crystallites (see Fig. 5.11 (c)). A further increase in selenization to 550°C resulted in a dramatic change in the morphological features of the films. These films (see Fig. 511 (d)) exhibited superior structural features and SEM studies revealed uniform and dense structures. Typically these films consisted of a high density of facetted grains with an average size of 1µm.

The influence of the selenization temperature on the crystalline quality of the films was also clearly revealed by XRD studies. It can be seen from Figs. 5.12 (a) to (c) that an increase in selenization temperature resulted in a systematic reduction in the volume fraction of binary phases, which corresponded to a more complete formation of the ternary alloys. The latter phenomenon was evident from the increase in the intensity of the characteristic [112], [220/204] and [312/116] peaks of the chalcopyrite lattice. It should be mentioned that XRD studies revealed minor changes in the crystalline quality of films selenized between 500°C and 550°C. Figure 5.12 (c) represents the typical crystalline quality of a film selenized in this temperature range. The total absence of binary phases indicated that the reaction process was completed after 60 minutes of processing at 550°C. It should also be noted that this process resulted in the formation of two separate ternary phases, i.e. CuInSe$_2$ and CuGaSe$_2$. The position of [112] diffraction peak of CuInSe$_2$ is close to 26.7°, while that of CuGaSe$_2$ is at higher angle
(i.e. 27.7°) due to reduction in the lattice parameter when In atoms are substituted by the smaller Ga atoms.
Fig. 5.11: SEM micrographs representing the morphological features of InSe/Cu/GaSe structures after reactive annealing in elemental Se vapour at (a) 300°C (b) 400°C, (c) 500°C and (d) 550°C for 60 minutes.
Fig. 5.12: XRD patterns of InSe/Cu/GaSe precursors after reactive annealing in elemental Se vapour at (a) 300°C (b) 400°C and (c) 550°C for 60 minutes. The XRD spectrum was measured with Cu Kα radiation (1.5418 Å).

The variation in the crystalline quality of the films as function of selenization temperature was also estimated from the full-width at half-maximum (FWHM) of the characteristic [112] and [220/204] diffraction peaks. In this regard it is important to keep in mind that the effective crystallite size is inversely proportional to the FWHM values of the diffraction peaks. Figure 5.13 (a) depicts the variation in the FWHM values for Mo/InSe/Cu/GaSe precursor structures, which were selenized for 60 minutes at temperatures between 200°C and 600°C. As expected, an increase in selenization temperature resulted in a sharp drop in the FWHM values, which corresponds to an increase in the average size in the crystallites present in the films. The degree of
preferred orientation of the thin films was also critically influenced by the selenization temperature.

Figure 5.13 (a): Variation in the FWHM values and (b) degree of preferred orientation of the films as function of selenization temperature.
It was recently indicated that the intensity ratio of the [112] diffraction peak with respect to the [220/204] peak (i.e. $I_{(112)}/I_{(220/204)}$) has a value of 1.5 in the case of randomly oriented films [Abernathy et al., 1984]. Figure 5.13 (b) clearly indicates that the $I_{(112)}/I_{(220/204)}$ intensity ratio varied strongly with the selenization temperature. Films selenized at low temperatures between 200°C and 400°C exhibited a preferred (112) orientation, while the orientation was mixed in the case of films selenized at 500°C. It is interesting to note that an increase in selenization temperature from 500°C to 600°C resulted in a sharp increase in the $I_{(112)}/I_{(220/204)}$ ratio. This phenomenon is probably related to a higher degree of recrystallization of the film at substrate temperatures above 500°C, resulting in the formation of faceted or columnar grain structures with a strong (112) preferred orientation. A typical example of such a film was shown in Figure 5.11 (d). It is important to mention that the tendencies presented in Figure 5.13 are representative and the specific data points represent average values obtained from various samples processed under identical conditions.

5.4.5 Influence of GaSe deposition temperature on the structural features and in-depth compositional uniformity of Cu(In,Ga)Se$_2$ thin films

5.4.5.1 Introduction

As indicated in Figs. 5.10 and 5.12, fully reacted Cu(In,Ga)Se$_2$ films were heterogeneous and consisted two separated ternary phases. The formation of the two distinct ternary phases (i.e. CuInSe$_2$ and CuGaSe$_2$) or graded material is the direct result of the segregation of gallium towards the Mo back contact during the high temperature selenization step. As pointed out in Section 5.4.3, this uncontrolled separation of phases occurred irrespective of the position of the GaSe layer in the
precursor structure prior to selenization. It should also be kept in mind that in these specific studies, the individual precursor layers (i.e. InSe, Cu and GaSe) were deposited at 200°C. In this part of the study, the stacking order of the precursor films (i.e. Mo/InSe/Cu/GaSe) was identical, while the deposition temperature of GaSe was varied. It was anticipated the deposition temperature of GaSe during the precursor formation stage would ultimately modify the diffusion behavior of Ga during the subsequent selenization step.

5.4.5.2 Structural features of films

For the purpose of direct comparison, the InSe and Cu layers were deposited at 200°C, while the GaSe films were deposited at 200°C, 300°C and 400°C. Figure 5.14 depicts the morphological features of various glass/Mo/InSe/Cu/GaSe structures in which the deposition temperature of the GaSe films was varied between 200°C and 400°C. It is important to realize that the final surface morphology of a specific sample is significantly influenced by the overall bulk composition of the film. Therefore, for the purpose of comparison, the depicted films in Fig. 5.14 had comparable bulk compositional properties, with Ga/(In+Ga) and Cu/(In+Ga) atomic ratios close to 0.25 and 0.8, respectively. These compositional values were achieved by maintaining the thicknesses of the InSe, Cu and GaSe layers at 1200 nm, 200 nm and 200 nm respectively. The observed variation in structural features observed in Fig. 5.14 is therefore directly related to the fact that the GaSe films were deposited at different substrate temperatures and not to variations in the bulk composition of the films. In the case where the total structure was deposited at 200°C, the InSe/Cu/GaSe precursor morphology was dominated by the presence of a high density of mostly rounded grains
(Fig. 5.14(a)), covering almost the entire layer surface. Typical grain sizes varied between 0.5 and 1µm. A similar structure was observed when the GaSe layers were deposited at 300°C (Fig. 5.14(b)) onto the InSe/Cu structures. In this case, however, the grain shapes appear to be more irregular and less dense.
Figure 5.14: Surface morphologies of typical glass/Mo/InSe/Cu/GaSe precursor structures. The relative thicknesses and positions of the respective layers were kept constant. The InSe and Cu layers were deposited at 200°C, while the GaSe layers were deposited at (a) 200°C, (b) 300°C and (c) 400°C.

A further increase in the GaSe deposition temperature to 400°C resulted in the formation of a completely different precursor alloy, composed mainly of large (1 to 3 µm) smooth-faced droplet-like crystallites in addition to other much smaller sub-micron grains in the background (Fig. 5.14(c)).

Fig. 5.15 depicts XRD patterns from the respective precursor films. In all cases, weak evidence of the CuInSe$_2$ (CIS) phase could be detected along with the expected binary-selenide phases. Strong evidence of InSe was detected in cases where the GaSe layers were deposited at 200°C and 300°C (Figs. 5.15(a) and (b)). In cases where the GaSe layers were deposited at temperatures around 400°C (Fig 5.15(c)), no evidence
of InSe was detected, but relatively strong evidence of both GaSe and CuSe binary phases. The (112) preferred orientation of CIS phase also became more prominent when the GaSe layers were deposited at 400°C in the precursor structure, confirming the expected higher degree of interaction between the binary phases at higher substrate temperatures.

Figure 5.15: XRD patterns from various Mo/InSe/Cu/GaSe precursor structures depicted in Fig. 5.14. The GaSe layers were deposited at substrate temperatures of (a) 200°C (b) 300°C and 400°C, while the other layers were deposited at 200°C.

The precursor films were simultaneously reacted to elemental Se vapour at 550°C for 60 minutes. XRF studies revealed no significant variation in the bulk composition (i.e., Ga/(In+Ga) and Cu/(In+Ga) atomic ratios) of films after selenization. However, SEM studies (see Fig. 5.16) revealed significant differences in the structural features of the final films due to variations in the deposition temperature of GaSe.
Figure 5.16: SEM micrographs of the selenized Mo/InSe/Cu/InSe precursors in elemental Se vapor at 550°C for 60 minutes. The precursors were simultaneously selenized and the GaSe layers were deposited at (a) 200°C, (b) 300°C and (c) 400°C during the precursor formation stage.

The influence of the precursor morphology on the structural features of the final selenized films is also clearly evident, especially in cases where the GaSe layers were deposited at 400°C during the precursor formation stage. A comparison of Figs 5.14(c) and 5.16(c) reveals how the two distinct regions (i.e. smooth-faced crystals and background region) of the precursor structure are transformed to the dominating morphological features of the Cu(In,Ga)Se₂ film after selenization. The smooth-faced crystallites of the precursor are represented after selenization by large conglomerates of smaller crystals, while the background material transformed mostly into 1 μm-size
faceted grains, interspersed between the large conglomerates. The selenized films depicted in Figs 5.16 (a) and (b) were clearly more homogeneous and consisted of densely packed, faceted chalcopyrite grains with typical sizes around 1\(\mu\)m. It is important to mention that the morphological features of the precursor structures and Cu(In,Ga)Se\(_2\) films, depicted in Figs 5.14 and 5.16, are representative and were confirmed by several growth studies.

XRD studies also revealed a dramatic variation in the crystalline quality of the films. In the case where all the layers were deposited at 200\(^\circ\)C, XRD studies revealed the presence of a graded CuIn\(_{1-x}\)Ga\(_x\)Se structure. The crystalline features of these specific films were discussed in detail in Section 5.4.3 and the relevant XRD pattern is depicted in Fig. 5.10. Figure 5.17 depicts a representative XRD pattern illustrating the crystalline quality of the films shown in Fig. 5.16 (b) and (c). It can be seen that a remarkable improvement in the crystalline quality was achieved when the GaSe films were deposited at temperatures above 200\(^\circ\)C. The extremely sharp, well-defined chalcopyrite peaks are indicative of the high crystalline quality of the ternary alloys. The fact that the diffraction peaks are symmetric also indicates that the film is uniform and monophasic rather than compositionally graded, as observed in Fig. 5.10. It is also important to note that the [112] peak position shifted towards a larger 2\(\theta\)-value (from about 26.65\(^\circ\) to 26.95\(^\circ\)). This shift of the chalcopyrite reflection is in accordance with a decrease in the lattice parameter associated with the homogeneous incorporation of gallium into the quaternary Cu(In,Ga)Se\(_2\) system. The degree of shift of the diffraction peak towards higher 2\(\theta\)-values is exactly in accordance with Vegard’s law, assuming single-phase material and a Ga/(Ga+In) atomic ratio close to 0.25.
Figure 5.17: Representative XRD pattern taken from the Cu(In,Ga)Se$_2$ films shown in Fig. 5.16 (b) and (c), clearly revealing sharp symmetric chalcopyrite peaks and the shift of the diffraction peaks to higher angles due to the homogeneous incorporation of gallium into the alloy.

5.4.5.3 In-depth compositional uniformity of samples

Figure 5.18( a) to (c) depict the in-depth compositional uniformity of the Cu(In,Ga)Se$_2$ films shown in Fig. 5.16 (a) to (c). These profiles were obtained according to the method described in Section 4.6.2.4. The resulting element concentrations of the respective samples as function of sample depth are also summarized in Tables 5.3 and 5.4. The indicated thickness values were calculated from the XRF measured total mass per area of the films divided by the density of Cu(In,Ga)Se$_2$. It is important to keep in mind that the etching profiles represent the compositional features of the material remaining after...
successive etching steps. The first three points on the broken lines to the right of the figures, for example, represent the bulk element concentrations of the unetched sample. A comparison of these profiles clearly demonstrates the variation in the in-depth compositional uniformity (i.e., Cu/(In+Ga) atomic ratio and Se concentration) for the selenized samples, in which the GaSe films were deposited at different temperatures. Fig. 5.18(a) depicts a typical etching profile from a Cu(In,Ga)Se$_2$ film, prepared by thermal evaporation of an InSe/Cu/GaSe precursor at 200$^\circ$C, and subsequently selenized at 550$^\circ$C for 60 minutes in Se vapor. Although the Se and Cu concentrations remained relatively constant through the depth of the sample, the In and Ga concentrations changed significantly. In this regard, it is important to note that the remaining material after the successive etching steps became increasingly In-poor towards the Mo back contact of the film, while the Ga concentration increased sharply in the same direction. This diffusion behaviour resulted in a variation in the Cu/(In+Ga) atomic ratio from around 0.8 to 0.6 through the film thickness (see Table 5.3). From these results it is reasonable to assume that this vertical compositional gradient resulted in the formation of a compositionally graded CuIn$_{1-x}$Ga$_x$Se structure. This observation is in agreement with XRD studies (see Fig. 5.10) and also confirms the observations of other workers [Marudachalam et al., 1997]. This diffusion behaviour was observed for all samples in which the GaSe films were deposited at low temperatures at or below 200$^\circ$C.
Fig. 5.18 (a): In-depth composition profile of a graded CuIn$_{1-x}$Ga$_x$Se structure in which all the layers in the precursor structure were deposited at a substrate temperature of 200°C. The XRD pattern of this specific film is shown in Fig. 5.10.

Fig. 5.18 (b) In-depth composition profile of a monophasic Cu(In,Ga)Se$_2$ film in which the top GaSe layer was deposited at a substrate temperature of 300°C. The XRD pattern of this specific film is shown in Fig. 5.17.
Fig. 5.18 (c): In-depth compositional profile of Cu(In,Ga)Se$_2$ film in which the GaSe layer was deposited at a substrate temperature of 400°C.

Fig. 5.18 (b) depicts the depth profile of a Cu(In,Ga)Se$_2$ film, prepared by the reactive annealing of a InSe/Cu/GaSe precursor in elemental Se vapour at 550°C for 60 minutes. In this case the GaSe film was deposited at 300°C during the precursor formation step. It is clearly evident that this deposition process resulted in Cu(In,Ga)Se$_2$ films with a high degree of in-depth compositional uniformity. The Cu/(In+Ga) atomic ratio remained virtually unchanged around 0.75 through almost the entire layer thickness. This observation is in agreement with Fig. 5.17, revealing single-phase Cu(In,Ga)Se$_2$ with no evidence of phase segregation. In the region close the Mo back contact, the Cu/(In+Ga) atomic ratio drops to approximately 0.7, mostly due to a slight decrease in Cu and increase in Ga concentration (see Table 5.4). The selenium content systematically increased from about 51 to 53 atomic percentage with sample depth. The
fairly large excess of Se through the entire thickness of this sample indicated that this specific film was over-selenized under the present reaction conditions. Deposition of GaSe at 400°C also resulted in selenized Cu(In,Ga)Se$_2$ films with a relatively high degree of in-depth compositional uniformity (see Fig. 5.18(c) and Table 5.5). The Se concentration through depth remained virtually unchanged around 51 at. %, while the Cu/(In+Ga) atomic ratio varied between 0.82 and 0.75. The Ga concentration increased slightly towards the Mo back contact region.

<table>
<thead>
<tr>
<th>Etching Step</th>
<th>Thickness (µm)</th>
<th>Film Mass (mg cm$^{-2}$)</th>
<th>Elemental Concentration</th>
<th>Atomic Ratio [Cu]/[In+Ga]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cu (at.%)</td>
<td>In (at%)</td>
</tr>
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<td>0.980</td>
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<td>19.32</td>
</tr>
<tr>
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<td>0.969</td>
<td>22.63</td>
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<tr>
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<td>0.445</td>
<td>20.71</td>
<td>13.25</td>
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</tbody>
</table>

Table 5.3: Summary of the in-depth XRF data presented in Fig 5.18(a), obtained from a repeatedly etched Cu(In,Ga)Se$_2$ sample in bromine methanol. Etching step 0 represents the bulk composition of the unetched sample.
Table 5.4: Summary of the in-depth XRF data presented in fig 5.18(b). In this case the GaSe layer was deposited at 300°C.

<table>
<thead>
<tr>
<th>Etching Step</th>
<th>Thickness (µm)</th>
<th>Film Mass (mg cm⁻²)</th>
<th>Element Concentration</th>
<th>Atomic Ratio [Cu]/[In+Ga]</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Cu (at.%)</td>
<td>In (at%)</td>
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<td>3</td>
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<td>0.42</td>
<td>0.25</td>
<td>18.93</td>
<td>19.83</td>
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</table>
Table 5.5: Summary of the in-depth XRF data presented in Fig 5.18(c). In this case the GaSe layer was deposited at 400°C.

<p>| | | | | | | |</p>
<table>
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<tr>
<td>7</td>
<td>0.48</td>
<td>0.262</td>
<td>20.78</td>
<td>19.09</td>
<td>8.51</td>
<td>51.62</td>
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5.4.6. The influence of gallium concentration on the structural and optical properties of Cu(In,Ga)Se$_2$

5.4.6.1 Introduction

It was indicated in the previous section that single-phase Cu(In,Ga)Se$_2$ thin films can be produced by the manipulation of the GaSe deposition temperature during the precursor formation step. This implies that a relatively simple two-step growth process can be used to produce quaternary absorber films in which the degree of gallium incorporation into the chalcopyrite lattice can be controlled. This in turn enables band gap engineering through precise variations in the lattice parameters of the absorber film. In this part of the study, single-phase Cu(In,Ga)Se$_2$ thin films with varying amounts of Ga were deposited. The shift in lattice parameters were determined from x-ray diffraction studies, while the corresponding variation in the band gap of the absorber films were calculated from optical measurements.
5.4.6.2 Influence of Ga concentration on the structural features of Cu(In,Ga)Se$_2$

It was indicated in the previous section that the diffusion behaviour of gallium in Cu(In,Ga)Se$_2$ thin films was critically related to the deposition temperature of GaSe. In order to obtain monophasic Cu(In,Ga)Se$_2$ thin films, the GaSe layers needed to be deposited at or above 300ºC, while the InSe and Cu layers were deposited at 200ºC. In order to reach a compromise between optimal structural and electrical properties, all films in this particular part of the study had Cu/(In+Ga) atomic ratios of approximately 0.9. In order to vary the Ga/(Ga+In) ratio, the relative thickness of InSe with respect to GaSe was varied. These precursor films were subsequently reacted to elemental Se vapor at 550ºC for 60 minutes. Fig. 5.19 depicts SEM micrographs of two selenized Mo/InSe/Cu/GaSe precursors with different gallium concentrations (x = Ga/[Ga+In] atomic ratio = 0.1 and 0.36). The bulk compositional properties of these films were determined by XRF studies. In both cases dense and uniform films were obtained. The film morphologies were characterized by the presence of large facetted chalcopyrite grains, which are typical for device quality material. It is important to note that an increase in gallium concentration resulted in a significant decrease in the average grain size of the film. This observation is in good agreement with other related studies [Arya et al., 1993, Al Bassam, 1998 and Pul et al., 1994].
Figure 5.19: SEM micrographs depicting the typical morphological features of single-phase (a) CuIn$_{0.9}$Ga$_{0.1}$Se$_2$ and (b) CuIn$_{0.64}$Ga$_{0.36}$Se$_2$ thin films.
Based on the SEM studies, it was anticipated that the crystalline quality of the CuIn$_{1-x}$Ga$_x$Se$_2$ thin films would be critically influenced by the gallium concentration in the bulk of the thin films (i.e. the value of $x$). In order to study this phenomenon in detail, films were prepared in which the value of $x$ was varied between 0 and 0.43. The overall bulk composition of the respective films were determined by XRF K$\alpha_{1,2}$ measurements, while the lattice parameters and relative crystallite sizes were estimated from XRD measurements. According to Vergard’s law there is a linear relationship in single-phase alloys between the lattice parameters and film composition. In the specific material system investigated in this study, a decrease in lattice parameters is expected when the gallium atoms replaces the indium atoms in the chalcopyrite lattice. Hence in the case of single-phase CuIn$_{1-x}$Ga$_x$Se$_2$ films the diffraction peaks would, according to Bragg’s law, shift to higher 2$\theta$-values as the gallium content increases. The theoretical and experimental values of lattice parameters single-phase CuIn$_{1-x}$Ga$_x$Se$_2$ films are tabulated in Table 5.6 (a) and (b) respectively. The theoretical variation of the lattice parameters for the chalcopyrite lattice were determined from Vegard’s law, while the experimental values were calculated from a fit to the experimental XRD data of Cu(In,Ga)Se$_2$. As expected, the lattice parameters $a$ and $c$ decreased linearly with increasing Ga content for values of $x$ between 0 and 0.43. There is also an excellent correspondence between the experimental and theoretical values, especially for low gallium concentration ($x \leq 0.32$). These results strengthen the claim that the reported deposition process produced single-phase quaternary alloys.
<table>
<thead>
<tr>
<th>Gallium concentration</th>
<th>Lattice parameter</th>
<th>Lattice parameter</th>
</tr>
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<tbody>
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<td>$x = \frac{Ga}{[Ga+In]}$</td>
<td>$a$ (Å)</td>
<td>$c$ (Å)</td>
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<tr>
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<tr>
<td>0.45</td>
<td>5.698</td>
<td>11.355</td>
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Table 5.6(a): Theoretical variation of the lattice parameters $a$ and $c$ in chalcopyrite alloys, predicted from Vegard's law for CuIn$_{1-x}$Ga$_x$Se$_2$ where $x$ varies between 0 and 0.45.
<table>
<thead>
<tr>
<th>Gallium concentration $x = \text{Ga}/[\text{In+Ga}]$</th>
<th>Lattice parameter $a$ (Å)</th>
<th>Lattice parameter $c$ (Å)</th>
</tr>
</thead>
<tbody>
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<tr>
<td>0.43</td>
<td>5.71</td>
<td>11.401</td>
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</table>

Table 5.6(b): Values of the lattice parameters $a$ and $c$ determined from a fit to the experimental XRD data of CuIn$_{1-x}$Ga$_x$Se$_2$ films for values of $x$ between 0 and 0.43.

Figure 5.20 depicts the variation in lattice spacing and full-width at half-maximum (FWHM) values of CIGS thin films as function of the Ga/(Ga+In) atomic ratio. The $d$-values were calculated from the $2\theta$ values of the [112] diffraction peaks, which are the most intense peaks of the chalcopyrite lattice. It is important to note from Fig. 5.20 that the lattice spacing $d_{(112)}$ of the alloyed compounds decrease linearly with an increase in the Ga/(Ga+In) atomic ratio. This behavior is related to the fact that gallium atoms are smaller than indium atoms and hence causes shrinkage of the lattice as they substitute indium sites in the cell. Even more significant, the linear dependence of the lattice spacing with gallium concentration implied that homogeneous CuIn$_{1-x}$Ga$_x$Se$_2$ alloys were produced for values of $x$ between 0.1 and 0.43. The positions of the [220/204] diffraction peaks for the respective samples are shown in Fig. 5.21, clearly indicating a
shift to higher diffraction angles due to the decrease in lattice parameters with increasing gallium concentration.

Figure 5.20: Graph depicting the dependence of the lattice spacing and FWHM values of the [112] diffraction peaks of a single-phase CIGS film on the gallium concentration.

Figure 5.21: Position of the [220/204] diffraction peaks of single-phase CuIn$_{1-x}$Ga$_x$Se$_2$ as function of gallium concentration.
Fig. 5.20 also depicts the variation in FWHM values of the (112) diffraction peaks as function of Ga content. It is important to keep in mind that the effective crystallite sizes are inversely proportional to the FWHM values of the diffraction peaks. In this regard, it is interesting to note that the FWHM values of the [112] peak decreased with increasing gallium concentration up to a Ga/(Ga+In) ratio around 0.25, which corresponds to an increase in the average grain size. However, a further increase in Ga content resulted in a dramatic broadening of the diffraction peaks and hence the subsequent sharp increases in the FWHM values. The observed increase in FWHM values above critical gallium concentrations corresponds to a decrease in the effective grain size with increased gallium incorporation into the chalcopyrite lattice. This degradation in crystalline quality of film with increasing Ga concentration ultimately impacts negatively on device performance of solar cell devices. It is also important to mention that this observation on a structural level is in line with reports from other groups, indicating a degradation in the electronic properties of CIGS films with high Ga/(Ga+In) ratios [Schafarman et al., 1996]. This phenomenon was attributed to a bias-dependent current collection due to reduced diffusion lengths of minority carriers and shortened space-charge region widths at Ga concentrations above 30%

5.4.6.3 Optical properties of Cu(In,Ga)Se$_2$ as function of Ga content.

Optical measurements were carried out with Cary UV-VIS-NIR spectrophotometer. Transmission (T) and reflection measurements (R) were taken of each relevant sample at room temperature in the wavelength range from 300-2000 nm. Using this data the absorption coefficient ($\alpha$) was calculated using the following expression:
where $t$ refers to the estimated thickness of the polycrystalline thin films. A detailed discussion of this theory was presented in Section 4.6.3.1. Fig. 5.22 (a) depicts plot of $(\alpha h\nu)^2$ vs $h\nu$ for a variety of films with increasing Ga content from left to right. The extrapolation of the linear portion of the $(\alpha h\nu)^2$ vs $h\nu$ graph at $\alpha = 0$ yields the band gap value of the material. The band gap of CuInSe$_2$ around 1eV agrees well with values generally reported values in literature [Schön et al., 1997a]. It can also be seen from Fig. 5.22(a) that the band gap values systematically increased to approximately 1.12 eV with an increase in the Ga/Ga+In ratio to values around 0.3. Although Vegard’s law predicts a linear shift for band gap with gallium concentration, it was experimentally observed that the $E_g$ versus Ga/(In+Ga) ratio (see Fig. 5.22(b)) exhibits a bowing behavior, which can mathematically be described as:

$$E_g(x) = E_1 + (E_2 - E_1 - b)x + bx^2,$$

(5.2)

where $E_1$ and $E_2$ are the band gap values of CuInSe$_2$ ($x = 0$) and CuGaSe$_2$ ($x = 1$) respectively, while $b$ is the bowing parameter. Curve fitting to the $E_g$ versus Ga/(Ga+In) ratio plot shows the following relation to be valid for our CIGS films:

$$E_g(x) = 0.998 + 0.390x + 0.430x^2,$$

(5.3)

where the bowing parameter is $\sim 0.430$. For $x = 1$ the above equation gives $E_g \sim 1.70$ eV, which agrees well with the expected band gap of CuGaSe$_2$. 

$$\alpha = \frac{2\ln(1 - R) - \ln(T)}{t},$$

(5.1)
Figure 5.22 (a): Plots of $(\alpha h\nu)^2$ vs $h\nu$ for CuIn$_{1-x}$Ga$_x$Se$_2$ films with increasing Ga content from left to right.

Figure 5.22(b) Variation in the band gap of CuIn$_{1-x}$Ga$_x$Se$_2$ films with increasing Ga content.
Figure 5.23 (a) shows the PL response of a device quality CuInSe$_2$ film deposited during this study. This specific film was prepared by the selenization of a glass/Mo/InSe/Cu/InSe precursor in elemental Se vapour at 550°C for 60 minutes. The structural features of this film were discussed in detail in Section 5.2.3. The Cu/In atomic ratio of this sample was 0.95.

Figure 5.23 (a): PL spectrum of a slightly In-rich CuInSe$_2$ thin film. The measurement was conducted at 4K.

The photoluminescence from this sample was dominated by the presence of a single peak at approximately 0.94 eV. This observation is in agreement with other studies indicating that the optical properties of slightly In-rich CuInSe$_2$ is dominated by the presence of a donor-acceptor-pair transition at about 0.95 eV [Schön et al., 1997b]. This
emission process is generally ascribed to the radiative transition between an electron and a hole bound to a selenium vacancy ($V_{Se}$) and a copper vacancy ($V_{Cu}$).

Figure 5.23 (b) depicts the optical properties of a polycrystalline Cu(In$_{0.7}$Ga$_{0.3}$)Se$_2$ thin film. These films were prepared under optimum growth conditions, as described in Section 5.4.6.2. Two peaks at 0.94 eV and 1.0 eV dominated the photoluminescence from these specific samples. The presence of the peak at higher energy is indicative of a small shift in the band gap of the absorber film due to the incorporation of Ga.

Figure 5.23 (b): PL spectrum of a Cu(In,Ga)Se$_2$ thin film. The presence of the peak at higher energy is attributed to the incorporation of gallium into the chalcopyrite lattice.
5.5 Device Fabrication and Analysis

5.5.1 Introduction

An important aspect of this study was the fabrication of completed solar cell devices based on CuInSe$_2$, CuIn(Se,S)$_2$ and Cu(In,Ga)Se$_2$ absorber layers. In order to achieve this goal it was important to optimize the material properties of the CdS buffer layers and ZnO window layers. The knowledge gained from this study was subsequently applied to produce completed devices. These devices were evaluated under standard conditions and the results are summarized in the following sections.

5.5.2 Material quality of CdS and ZnO

Figure 5.24 depict the typical optical transmission spectra for the CdS films with different thicknesses. The experimental procedures followed during the deposition of the CdS buffer layers were discussed in detail in Section 4.5.1. For the purpose of comparison, the transmission spectrum of an uncoated glass substrate is also shown. The CdS films were deposited for 5 minutes, 5.5 minutes and 6 minutes respectively. The transmission spectra were measured with a Varian Cary 500 spectrophotometer in the wavelength range between 250 and 2500 nm. This range covers the ultraviolet to near-infrared portion of the spectrum. It is important to note that very high transmission values around 90% was obtained for all three films in the region between 1300 and 2500 nm. The increase in deposition time from 5 minutes to 6 minutes resulted in an increase in CdS thickness, which is clearly evident by the substantial drop in transmission in the shorter wavelength region between 600 and 1000 nm. The sharp cut-off around 550nm (about 2.4 eV) corresponds to the optical band gap of CdS.
Figure 5.24: Typical transmission spectra of CdS films grown for a) 5 minutes, b) 5.5 minutes and c) 6 minutes on glass. For comparison, the transmission spectrum of clean uncoated glass is represented by curve 0.

The transparent conducting ZnO films were magnetron sputtered from ceramic ZnO and ZnO:Al$_2$O$_3$ targets, as described in Section 4.5.2. The optical and electrical properties of the ZnO films were critically influenced by the degree of doping and substrate heating. Fig 5.25 a) depicts the typical optical transmission spectrum of an intrinsic ZnO thin film, deposited at about 200°C on glass. In general these undoped ZnO films with typical thicknesses around 50 nm exhibit high transmission values above 80% over a broad range of the spectrum. Once again, the sharp dip in the transmission (i.e. increase in absorption) around 350nm corresponds to the band gap edge of ZnO. The doped sample (Fig. 5.25.b)) with typical thickness around 500 nm exhibited high transmission
values in the short wavelength region between 500 and 800nm, while a dramatic drop in transmission was observed in the region between 1000 and 2500 nm.

![Graph showing transmission spectra](image)

Figure 5.25: Transmission spectra of a) intrinsic and b) Al-doped ZnO films grown by RF magnetron sputtering at substrate temperatures close to 200°C.

This phenomenon is explained by taking into account that doping resulted in a dramatic increase in the free carrier concentration. The resulting increase in the free carrier absorption in the case of doped samples resulted in a steep decrease in the transmission from about 80% around 900 nm to about 60% at 1200 nm and to below 10% at 2000 nm. The oscillatory behaviour of curve 5.25 (b) is due to the interference between the incoming and reflected light. The electrical properties of the intrinsic and doped ZnO were investigated by four-point probe measurements. The sheet resistances of the doped and intrinsic samples were 20 Ω/square and above 300
\( \Omega \)/square respectively. However, it should be mentioned that the low sheet resistance of doped samples could only be achieved with proper substrate heating.

Figure 5.26 depicts the typical optical properties of a 50nm thick undoped ZnO film deposited onto CdS layers with various thicknesses. The thicknesses of the CdS films were controlled by the dip period and were varied as indicated in Fig. 5.24.

Figure 5.26: Transmission spectra of various CdS/ZnO structures deposited onto glass. The ZnO thickness was kept constant around 50 nm, while the CdS layer thicknesses were varied by increasing the dip period from a) 5 minutes, b) 5.5 minutes and c) 6 minutes.

It is interesting to note that the combined CdS/ZnO structures exhibited high transmission values between 70-80\% for a large portion of the spectrum, which is an important prerequisite for achieving high current generation by the completed devices.
Low absorption losses in the buffer/window layer imply that a high percentage of incoming light photons would reach the CIS absorber layer in order to generate charged carriers. These results therefore indicate that the CdS/ZnO structures were optimized and in combination with device quality absorber films should yield efficient devices.

5.5.3 Device analysis

Heterojunction solar cells were fabricated and evaluated under simulated AM 1.5 (100 mW/cm²) conditions at 25°C. The typical device structure is depicted in Fig. 2.6, and the respective processing steps were discussed in detail in Sections 4.5. In short, the absorber films were immediately after deposition coated with a 50 nm thick CdS buffer layers. The CdS layer was then covered with a 50 nm highly resistive intrinsic ZnO layer, followed by a highly doped n-type ZnO film with typical thickness around 500 nm. The material quality of these specific films was summarized in the previous section. The 50 nm Ni/1 µm Al front contacts were deposited by electron-beam evaporation onto the ZnO without any intentional heating of the substrate. The perimeters of individual cells were then mechanically scribed to yield device areas of approximately 0.5 cm².

The characteristic JV curve of a glass/Mo/CuInSe₂/CdS/ZnO solar cell device is shown in Fig. 5.27. The absorber film in this case was prepared by the reaction of a Mo/InSe/Cu/InSe precursor to elemental Se vapour at 550°C for 60 minutes. The material properties of these films were discussed in detail in Section 5.2.3.
The open-circuit voltage ($V_{oc}$) value typically varied between 300 and 410mV, depending on the quality of the absorber film. The short-circuit current densities ($J_{sc}$) varied between 25 and 35mA/cm$^2$, while the fill factor (FF) values were limited to between 40 and 60%. These relatively low fill factor values are attributed to fairly high shunt resistances present in the device, and limited the conversion efficiencies of these specific devices to around 8%. The replacement of the CuInSe$_2$ absorber film with a CuIn(Se,S)$_2$ film yielded marginal improvements in conversion efficiencies with typical $V_{oc}$ values still well below 500mV. These low voltage values indicated that the incorporation of S into the CuInSe$_2$ absorbers did not result in a detectable increase in the band gap.

Figure 5.28 depicts a typical illuminated curve of a glass/Mo/Cu(In,Ga)Se$_2$/CdS/ZnO device. In this case, the absorber film was produced by annealing a
glass/InSe/Cu/GaSe precursor in elemental Se vapour at 550°C for 60 minutes. In order to produce monophasic Cu(In,Ga)Se₂ absorbers with a modified band gap, the GaSe films were deposited at temperatures at or above 300°C. The structural and optical features of these specific films are summarized in Sections 5.4.6.2 and 5.4.6.3 respectively.

It is important to note that in these cases open-circuit voltages above 500mV were achieved, which is directly related to the increase in the band gap of the absorber film due to the homogeneous incorporation of Ga into the chalcopyrite lattice. This result is in agreement with the reported good crystalline quality of the absorber film (see Fig. 5.19). With fill factor values around 70% and short-circuit current density close to 30mA/cm², conversion efficiencies above 10% were reached.

Figure 5.28: Typical illuminated J-V characteristics of a glass/Mo/Cu(In₀.₆₄Ga₀.₃₆)Se₂/CdS/ZnO solar cell device fabricated during this study.
Figure 5.29: (a) External quantum efficiency of a solar cell, fabricated with a CuInSe$_2$ absorber film and (b) plot of $(QE \times h\nu)^2$ versus energy, indicating a band gap value of 1.0 eV.
Figure 5.30: (a) External quantum efficiency of a solar cell, fabricated with a Cu(In,Ga)Se$_2$ absorber film and (b) plot of (QE$\times$h$\nu$)$^2$ versus energy, indicating an increase in band gap due to the incorporation of Ga into CuInSe$_2$. 
Figure 5.29 (a) depicts the typical photoresponse of a solar cell produced with a CuInSe\(_2\) absorber film. The dip in the quantum efficiency at short wavelengths at approximately 500nm is due to absorption in the CdS and ZnO layers, while the long wavelength cut-off corresponds fairly well with the absorption edge of a CuInSe\(_2\) thin film. The maximum quantum efficiency yield of 87% was obtained at \(\lambda = 560\)nm. The overall response is relatively flat, indicating a sufficiently large collection width (i.e. space charge region plus diffusion length). However, significant losses at long wavelengths (900 –1200 nm) were normally observed in the case of these specific cells. Figure 5.29 (b) shows a plot of \((\text{QE} \times h\nu)^2\) versus energy, obtained from Fig. 5.29 (a). From this plot a band gap value of 1eV was obtained which is in excellent agreement with the optical results presented in Fig. 5.22 (a).

The quantum efficiency of a Cu(In\(_{0.64}\)Ga\(_{0.36}\))Se\(_2\)/CdS/ZnO cell is shown in Fig. 5.30 (a). Once again the cut-off at short wavelength around 500 nm is due to absorption in the window layer. In these cells, a maximum quantum efficiency yield of 92.8% was achieved at \(\lambda = 622\) nm. It is also important to note that the extrapolation of the linear portion of the \((\text{QE} \times h\nu)^2\) versus \(h\nu\) graph at QE = 0 yields the band gap of 1.18 eV, which once again confirmed that the homogenous incorporation of Ga into CuInSe\(_2\) resulted in an increase in band gap. This result is in agreement with the optical results presented in Fig. 5.22 (a). This increased band gap value in turn resulted in a substantial increase in the open-circuit voltage of the device as depicted in Fig. 5.28.
Reference


