Recrystallization of Cu(In,Ga)Se$_2$ thin films studied by X-ray diffraction

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Abstract: A recrystallization is essential for the synthesis of highest quality Cu(In,Ga)Se$_2$ (CIGSe) thin films for solar cell applications. Here we present a real-time study of the recrystallization of CIGSe thin films. We trigger the recrystallization by allowing diffusion of Cu into a Cu-poor CIGSe film and use synchrotron-based energy-dispersive X-ray diffraction to monitor this transition in real time. Additionally, we characterize the films by means of angle-dispersive X-ray diffraction. Before recrystallization, the X-ray diffraction patterns exhibit a diffraction maximum that does not correspond to the ideal chalcopyrite structure of CIGSe. We attribute this maximum to stacking faults within the bulk of the films by modeling diffraction patterns of faulted CIGSe with the software DIFFaX. This diffraction maximum is detected at temperatures below 650 K and is absent at temperatures above 750 K, indicating that the faults in question were annihilated in this temperature range. This process occurs after the incorporation of Cu into the Cu-poor CIGSe lattice which takes place in the 550K to 650K temperature range. © 2013 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved. Doi: 10.1016/j.actamat.2013.04.006

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1. Introduction

Cu(In,Ga)Se$_2$ (CIGSe) based thin-film solar cells present power conversion efficiencies of up to 20%[1]. So far, the best CIGSe materials have been fabricated by means of a three-stage evaporation process from elementary material sources [2]. In these processes, a Cu-poor material ([Cu]/([Ga]+[In]) < 1), is deposited first. Cu is then deposited in a Se atmosphere until the films become Cu-rich ([Cu]/([Ga]+[In])>1). At this stage, a process commonly referred to as recrystallization, takes place near the point where the Cu(In,Ga)Se$_2$ stoichiometry is achieved ([Cu]/([Ga]+[In])=1). It is generally accepted that such a recrystallization is necessary in order to achieve high efficiency solar cells [3, 4, 5]. However, it remains unclear how the microstructure of the deposited thin films change during this recrystallization. Barreau et. al. observed a change of the preferred orientation before and after the stoichiometry point and concluded that grain boundary motion plays a crucial role during recrystallization[4]. Caballero et. al. showed that CIGSe films that were close to the stoichiometry point but still Cu-poor already presented large grain sizes[5]. These films lead to solar cells with low open circuit voltages. Therefore they concluded that grain growth, and thus grain boundary motion, is not a sufficient condition for high solar cell efficiencies. During recrystallization, other not yet identified defects have to be removed from the grains in order to achieve high efficiency. This paper points to a possible candidate for the defects in question.

We designed a model experiment where the recrystallization could be isolated from the film growth. For this we prepared layer stacks consisting of: a bottom layer of a Cu-poor CIGSe film
([Cu]/([In]+[Ga])<1) which had not been Cu-rich and therefore no recrystallization had occurred before, and a top layer consisting of Cu-Se deposited at low temperatures and leading to an overall composition of the stack such that [Cu]/([In]+[Ga])>1. The recrystallization of the CIGSe film is triggered when Cu diffuses into the Cu-poor CIGSe film during a subsequent heating process. We monitor this recrystallization by recording the changes in the diffraction signals in real time. Microstructural changes during the recrystallization are identified by analysis of the diffracted signals and comparison of measured to simulated diffraction patterns. On the basis of these studies we are able to discriminate between the different steps of the recrystallization process.

2. Experimental

Thin CIGSe films were deposited on Glass/Na-barrier/Mo substrates following a three-stage recipe as explained in [4] with a maximum substrate temperature of 870 K. The fabrication process was interrupted at [Cu]/([Ga]+[In])≅0.79 before the films reached the Cu-rich stage of the three-stage fabrication process, i.e. before recrystallization took place. These films will be referred to as precursor films in the following. The precursor films were then transferred to a second evaporation chamber where Cu-Se was deposited without intentional substrate heating. The resulting CIGSe/Cu-Se bilayer stack had an overall composition such that [Cu]/([Ga]+[In])≅1.09. The compositions of the films were determined by X-ray fluorescence analysis (XRF). The results of the analysis are shown in Table 1.

Table 1: Elemental concentrations (±1 at.%) of the films for the model experiment

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu / at. %</th>
<th>In / at. %</th>
<th>Ga / at. %</th>
<th>Se / at. %</th>
<th>Cu/In+Ga</th>
<th>Ga/In+Ga</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIGSe Precursor</td>
<td>23</td>
<td>19</td>
<td>10</td>
<td>50</td>
<td>0.79 ± 0.09</td>
<td>0.34 ± 0.03</td>
</tr>
<tr>
<td>CIGSe/Cu-Se Bilayer</td>
<td>25</td>
<td>14</td>
<td>9</td>
<td>53</td>
<td>1.09 ± 0.14</td>
<td>0.39 ± 0.04</td>
</tr>
</tbody>
</table>

The CIGSe/Cu-Se bilayer and the CIGSe precursor layer (reference experiment) were then heated in vacuum (background pressure <1x10⁻² Pa) to 850 K at a constant rate of 28 Kmin⁻¹. To avoid Se loss during heating the films were placed in an evacuated but sealed graphite reactor within the chamber. The temperature was measured by a thermocouple placed above the samples. This chamber was designed to allow the recording of energy-dispersive X-ray diffraction (EDXRD) spectra in real time at the EDDI beamline of the BESSY II synchrotron facility. Details of the beamline, the vacuum chamber and the experimental setup can be found in [6, 7]. The diffraction angle for the experiments was 2θ=6.3 °. The analyzed film area was approximately 1 x 5.4 mm². The position of the films was kept constant within the analyzed volume during heating by monitoring the maximum intensity of the Mo Kα line coming from the Mo-coating of the substrate. To complete the characterization, the films were analyzed with angle-dispersive X-ray diffraction (ADXRD) using an X-pert PRO MRD equipment from Panalytical in the Bragg-Bentano configuration. We used an Empyrean X-ray tube with a Cu anode (line focus and tube voltage and current of 45 kV and 40 mA) and a PIXcel 3D detector in the line scanning mode. Divergence and anticratter slits of 1/2 ° and 1 ° were used together with a 0.04 rad soller slit in the incident beam optics. 0.04 rad soller slit and a Ni filter were used in the diffracted optics. 2theta-omega scans were performed in the 22 ° to 32 ° range with a step size of 0.01° and total scan time of about 8 hours. Data treatment consisted in the addition of three adjacent data points while lowering the resolution to 0.03°, fitting the background with a fourth order polynomial function and normalization. The microstructure of the films was also characterized in a Quanta 650 FEG scanning electron microscope (SEM) from FEI equipped with a detector for energy-dispersive X-ray emission (EDX) analysis.

3. Modeling of diffraction patterns

Modeling of ADXRD patterns was performed using the software DIFFaX [8]. DIFFaX is capable of modeling ADXRD patterns of layered structures. We use a simplified structural model of CIGSe. The modeled CIGSe phase is cubic, has a lattice parameter of 0.5704 nm and is composed of two cubic
face centered sublattices, one for the Se anions and one for the Cu, In and Ga cations. This simplification allows a straightforward transformation into a layered structure since the cubic face centered sublattices can be seen as stacks of layers in the [111] direction stacked with an ABCABC type stacking. The group III positions are occupied to 70% by In and to 30% by Ga cations. Additionally, we model a random distribution of the cations by assuming a 50% occupation of group I and group III cations on every cation position. The diffraction patterns were modeled for the X-ray radiation energy of Cu-Kα1 (8048 eV).

4. Results

4.1 Ex-situ characterization before and after recrystallization

The average grain size of the CIGSe/Cu-Se bilayer increased as a result of the heating process as shown in Figure 1. EDX analysis suggests that Cu diffused from the surface of the film into the CIGSe layer during the heating (Figure 2). The final state still shows a segregation of Cu at the surface. No other significant segregation of elements can be seen in Figure 2.

Figure 1: Secondary electron micrographs of cleaved cross-sections of the CIGSe/Cu-Se bilayer before (a) and after (b) heating to 850K.

Figure 2: EDX intensities of cleaved cross-sections of the CIGSe/Cu-Se bilayers before (a) and after (b) heating to 850K. The acceleration voltage was 7 kV.
Figure 3a shows ADXRD patterns in the angular range from 25° to 29° of (from top to bottom): the CIGSe precursor before heating, the CIGSe precursor after heating (reference experiment), and the CIGSe/Cu-Se bilayer after heating. The films were previously etched with KCN to eliminate any contribution of Cu-Se phases. The figure also presents the expected positions and intensities of the 112 and 103 maxima of Cu(In$_{0.7}$Ga$_{0.3}$)Se$_2$ according to the card 35-1102 of the international centre of diffraction data (ICDD). The position of the measured 112 and 103 diffraction maxima are shifted with respect to the reported maxima due to the higher Ga content of the films studied here: [Ga]/([In]+[Ga]) of 0.34 to 0.39 instead of 0.3 of the reference (see [9] for the dependence of the lattice parameters of CIGSe on the Ga content). Surprisingly, a maximum (A) which is not expected to appear in the ideal chalcopyrite structure is seen at 25.55° (0.349 nm) in the CIGSe film before heating. It is important to note that this maximum is still visible in the CIGSe film after heating (reference experiment). This maximum has disappeared in the CIGSe/Cu-Se film after the heating process. Therefore, the structural features responsible for this maximum were annihilated as a result of the heating process of the CIGSe/Cu-Se bilayer.

Figure 3: a) ADXRD patterns of: the CIGSe precursor before heating, the CIGSe precursor after heating to 850K (reference experiment) and the CIGSe/Cu-Se bilayer after heating to 850K. The films were previously etched with KCN to eliminate any contribution of Cu-Se phases. The top axis indicates the corresponding lattice spacings, according to the diffraction conditions. b) ADXRD patterns of faulted chalcopyrite CIGSe simulated with the software DIFFAX [8]. The patterns correspond to a simplified CIGSe structure with: 6% twin faults, 6% extrinsic faults and with vanishing fault concentrations. The grey pattern on the top graph corresponds to a slightly increased Ga concentration. The dashed lines correspond to patterns with complete disorder on the cation sublattice. The top axis indicates the corresponding lattice spacings according to the simulated diffraction conditions. The bottom graphs present the expected positions and intensities of the 112 and 103 maxima of Cu(In$_{0.7}$Ga$_{0.3}$)Se$_2$ according to the ICDD card 35-1102.
4.2 Modeling the effect stacking faults on the diffraction pattern

To investigate the origin of the diffraction line noted as A in Figure 3a we model ADXRD patterns of the CIGSe chalcopyrite phase containing stacking faults as described in section 3. Figure 3b shows calculated ADXRD patterns of the simplified CIGSe structure. The third graph from top to bottom corresponds to a vanishing stacking fault concentration of 0.1%. The CIGSe 112 and 103 diffraction maxima are seen at about 27.07° and 28.25°. According to the definitions given in [10], we introduce in the structural model twin (ABC-BCA) or extrinsic (ABC BABC) stacking faults in the [111] direction of the cubic structure, which corresponds to the [221] direction of the chalcopyrite structure. We find that stacking faults result in a modified diffraction profile and in the appearance of a diffraction maximum at about 25.55° (or 0.349 nm) which is noted as A in the first two patterns of Figure 3b. The best qualitative fit of the experimental data was obtained when introducing a 6% concentration of stacking faults in the structure. The dashed lines in the Figure 3b correspond to the same faulted structures but with complete disorder in the cation sublattice. Therefore the observed features, do not depend on the ordering of the cations in their sublattice. Also, increasing the [Ga]/([Ga]+[In]) ratio to 0.35 while maintaining the same simplified structure does not have a significant effect on the normalized calculated pattern (grey pattern on the top graph of Figure 3b). The observed features only depend on the amount and type of faults in the structure. Figure 4 presents the effect of a variation of the concentration of twin stacking faults on the ADXRD pattern of CIGSe. Modeling the ADXRD patterns of faulted CIGSe predicts the position and profile of the measured 112, 103 and the diffraction maximum noted as A in Figure 3a. A modified 112 diffraction profile may also be caused by inhomogeneous strain or domain size effects [11]. However the presence of a supplementary diffraction maximum cannot be explained by such features. Therefore we attribute the diffraction maximum A to the presence of stacking faults in the [221] direction of the chalcopyrite structure. We note that a low intensity maximum but closer to the 112 Bragg reflection was reported by Guo et. al. [Guo] in CuInSe$_2$. They attributed this maximum to stacking faults, though in another crystalline direction. It is possible that our thin films also present different types of stacking faults. However we believe that those in the [221] direction are predominant in our case since they can originate in the phase transformations during the films formation as will be presented in the Section 5.

Figure 4: ADXRD patterns of faulted CIGSe as a function of the concentration of twin stacking faults $\alpha$ simulated with the software DIFFaX [8].
4.3 Real-time experiments

To identify the temperature at which the diffraction signature attributed to stacking faults disappears and to correlate this to the incorporation of Cu we recorded EDXRD signals during the annealing of the CIGSe/Cu-Se bilayer stacks. Normalized EDXRD spectra during heating of the bilayer are shown in Figure 5a. Besides the CIGSe 112 reflection the diffraction lines corresponding to CuSe 006 and Cu$_{2-x}$Se 111 are visible (figure 5a and 5b). These lines are lacking during the heating of the CIGSe precursor film in the reference experiment (not shown). The phase transition CuSe to Cu$_{2-x}$Se starts at about 550 K. This phase transition is characterized not only by the appearance of the Cu$_{2-x}$Se reflections, but also by a decrease of the normalized Se Kα fluorescence signal, in contrast to the normalized In Kα signal (Figure 5c). This is in agreement with the evaporation of Se following the reaction

$$2\text{CuSe} \rightarrow \text{Cu}_2\text{Se} + \text{Se}(g)$$  \hspace{1cm} (1)

Figure 5a also presents the positions in the energy scale of the diffraction maxima extracted by multiple-line fitting of the data. The CIGSe 112 line was fitted with a pseudo-Voigt profile, whereas all other reflections, which present a lower intensity, were fitted with Gaussians with fixed widths. The CIGSe 112 line is detected at all temperatures. A Cu$_{2-x}$Se 111 diffraction line is detected starting at 550 K. At temperatures higher than 650 K the data is best fitted when a low-intensity maximum is included at about 34 keV. It is possible that this maximum originates from a second Cu$_{2-x}$Se phase with a different composition within its homogeneity range \[12\]. Within this range, Cu$_{2-x}$Se shows different lattice parameters and expansion coefficients depending on the composition. Correspondingly, the expected positions of the Cu$_2$Se 111 and Cu$_{1.77}$Se 111 diffraction maxima are
plotted as continuous lines in Figure 5a according to the extrapolation of the data from Tonejc [13]. However, it is also possible that this maximum stems from another phase of the type (Cu,In,Ga)$_{2-x}$Se where small amounts of In or Ga are dilute in the Cu$_{2-x}$Se lattice [14]. We cannot unambiguously attribute this maximum to the first or second possibility. For the sake of simplicity we note these two maxima Cu$_{2-x}$Se 111.

We use the expansion of the 112 lattice spacing to narrow down the temperature range in which Cu is incorporated into the CIGSe lattice. As the Cu content increases within the chalcopyrite CIGSe, the lattice parameters increase. At room temperature and a similar [Ga]/([In]+[Ga]) of 0.25, the 112 lattice plane distances are 0.3303 nm and 0.3312 nm for chalcopyrite CIGSe with [Cu]/([In]+[Ga]) of 0.8 and 0.9 respectively [15]. This implies an expansion of 0.3% as the composition becomes Cu-richer within this range. Therefore in our experiment the increase of the lattice parameters during the incorporation of Cu will be superimposed to the thermal expansion. Accordingly, the temperature range in which the measured lattice expansion deviates from the thermal expansion of CIGSe corresponds to the range in which Cu is effectively incorporated into the chalcopyrite CIGSe lattice.

To narrow down the temperature range in which Cu is introduced into the CIGSe lattice, we extract first the lattice parameter $d_{112}$ from the positions in the energy scale, $E_{112}$, of the CIGSe 112 maximum using the energy-dispersive Bragg equation

$$d_{112} = \frac{hc}{2\sin(\theta) E_{112}}$$

(2)

with $h$ planck’s constant, $c$ the speed of light and $\theta$ half the diffraction angle. Using the lattice parameter, we then define the temperature-dependent expansion of the 112 planes, noted as $\eta_{112}$, using the formula

$$\eta_{112}(T) = \frac{\Delta d_{112}(T)}{d_{112}(T) \cdot \Delta T} = \frac{d_{112}(T + 1/2\Delta T) - d_{112}(T - 1/2\Delta T)}{d_{112}(T) \cdot \Delta T}$$

(3)

where $d_{112}$ is the lattice parameter, $T$ the temperature and $\Delta T$ the temperature step. We note that $\eta$ differs from the conventional thermal expansion coefficient in that it gives the instantaneous variations of the lattice planes as a function of temperature instead of a cumulative variation relative to room temperature. The time-dependent values of $\eta_{112}$ for both the CIGSe/Cu-Se bilayer and the CIGSe precursor layer (reference experiment) are plotted in Figure 5d. It can be seen that in the 550 K to 650 K temperature range, $\eta_{112}$ of the CIGSe/Cu-Se bilayer deviates from the behavior of $\eta_{112}$ of the CIGSe precursor layer. We attribute this to the incorporation of Cu into the CIGSe lattice during the heating of the CIGSe/Cu-Se bilayer. Once no further Cu can be introduced in the lattice, the measured expansion falls down to the level of the thermal expansion of the CIGSe precursor layer.

We note that the diffraction maximum A, which was found in the ADXRD data of Figure 3, cannot be clearly identified in the color-coded representation of the EDXRD data of Figure 5a due to its low intensity. This maximum can only be seen after summing up several sequentially recorded spectra. EDXRD data summed up over different temperature ranges and the corresponding multiple-line fits are shown in Figure 6. The diffraction maxima correspond to lattices spacings that are larger than the ones seen in Figure 3. This is attributed to the thermal expansion which is clearly seen in Figure 5a. The maximum A is detected at about 32.5 keV and is present up to a temperature of 750 K. Above this temperature the maximum A disappears and the width of the 112 signal decreases. Therefore the structural features responsible for this diffraction line were annihilated in the 650 K to 750 K temperature range.
5. Discussion

We show that during heating of the CIGSe/Cu-Se bilayer a recrystallization took place. Morphologically this is seen by an increase in grain size. However, other than grain growth, our data and modeling suggest that stacking faults were also annihilated during this process. Stacking faults have been observed before in CdTe and CIGSe-chalcopyrite films by means of transmission electron microscopy [16,17,18]. It is also known that during the fabrication of chalcopyrite CIGSe films by means of the three-stage evaporation process the Se sublattice must change from the hexagonal sublattice of the $\gamma-(\text{In,Ga})_2\text{Se}_3$ phase to the tetragonal sublattice of Cu(In,Ga)Se$_2$ phase [19]. Therefore, the stacking of the Se layers evolves in a series of phase transitions from an ABABAB-type stacking to an ABCABC-type stacking. In the CuIn$_5$Se$_8$ phase, which lies between In$_2$Se$_3$ and CulnSe$_2$ in the pseudo-binary In$_2$Se$_3$-Cu$_2$Se phase diagram [14], the Se stacking can be seen as an organized arrangement of stacking faults [20]. Therefore it is not surprising if stacking faults remain if these phase transitions cannot occur fully. However, it is surprising that these stacking faults are only annihilated if additional Cu is incorporated into the Cu-poor CIGSe lattice as we find in this study. It
is known that near the point where no further Cu can be incorporated into the chalcopyrite CIGSe lattice, the point defect concentration changes [21] and Cu-Se aggregates form [22]. It is yet to be clarified how these phenomena are connected to the annihilation of stacking faults. Further characterization is also necessary to assess the effect of the different types of stacking faults on the minority carrier recombination and hence on the device performance.

6. Conclusion

We presented electron microscopy and X-ray diffraction data revealing microstructural changes during the recrystallization of chalcopyrite CIGSe films for high efficiency solar cells. We modeled the effect of stacking faults on the diffraction patterns of CIGSe. The diffraction data and the modeling suggest that, other than grain boundary motion, the recrystallization of CIGSe thin films includes the annihilation of stacking faults within the grains. Furthermore, we find that the annihilation of these faults occurs only after the incorporation of Cu into the Cu-poor CIGSe chalcopyrite lattice.

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References


