Cu-dependent phase transition in polycrystalline CuGaSe₂ thin films grown by three-stage process

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I. INTRODUCTION

Chalcopyrite Cu(In,Ga)Se₂ (CIGS) is one of the most promising materials to realize a high-efficiency, low cost thin film solar cell. An efficiency of 19.9% has already been achieved for the CIGS-based solar cell. Deviation from the ideal stoichiometry of this material is reported to form some secondary phases, preferably segregated on the surface of the material. Therefore, an intensive study becomes indispensable to understand the proper physics and growth conditions for the ODC phase formation in this material. In this study, we have systematically grown several CuGaSe₂ thin films by changing the Cu content in the bulk of the film. A Cu-deficiency parameter, Z, which is defined as \( Z = (1 - Cu/Ga) \), has been used to determine the deviation of the film from the stoichiometric composition of CuGaSe₂ (1:1:2) composition. Thus, with an increase in the Z-value, the sample becomes more Cu-rich and Ga-rich while for Z < 0, the sample becomes Cu-poor. In this report we focus on the investigation of the evolution of various Cu-poor phases in CuGaSe₂ thin films as a function of the Cu-deficiency parameter, Z. The phase transition along the depth of the CuGaSe₂ samples has also been studied.

II. EXPERIMENTAL

Polycrystalline CuGaSe₂ thin films with the typical thickness of 2 \( \mu \)m were grown over Mo-coated soda lime glass substrates through a three-stage co-evaporation process using a molecular beam epitaxy system. Evaporation was performed at a base pressure of approximately \( 1 \times 10^{-6} \) Pa from three Knudsen-cells (K-cells) that were the respective Cu, Ga, and Se sources. The growth temperature of the first stage was kept at 400 °C during the co-evaporation of the Ga and Se. The temperature was increased to 520 °C at the second and third stages when the Cu, Se, and Ga, Se co-evaporation was done, respectively. To obtain the uniform composition of the films, the substrate was kept in a constant rotation of 10 rpm during deposition. All of the samples were grown at the constant flux rate of Cu, Ga, and Se. Several CuGaSe₂ films with various bulk Cu-deficiency parameters, Z \( \equiv (1 - Cu/Ga) \), have been fabricated by changing the third stage growth time. The composition of the grown films was measured by electron probe micro-analyzer (EPMA) and the synchrotron x-ray diffraction method. A Cu-deficiency parameter, Z, defined as \( (1 - Cu/Ga) \), was used to study the phase transition. Upon increasing the Z-value, the composition of the films on the Cu₂Se-Ga₂Se₃ pseudo binary tie line was found to shift from the stoichiometric CuGaSe₂ (1:1:2) (\( Z = 0 \)) to the Ga-rich composition through the formation of several ordered defect compounds. The structural modification in the Cu-poor CuGaSe₂ film has been investigated by the synchrotron x-ray diffraction method. The existence of the Cu-poor surface phase over the near-stoichiometric bulk CuGaSe₂ film was confirmed by the fitting of the accelerated voltage dependent EPMA data.

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III. RESULTS AND DISCUSSIONS

Figure 1 shows the elemental composition of several CuGaSe$_2$ thin films measured as a function of the Cu-deficiency parameter, Z, in the film. The composition of the films, as shown in Fig. 1 was measured by EPMA at 15 kV of the acceleration voltage, which corresponds to the composition information around the depth of 500 nm inside the film. Therefore, we can discard the effect of surface roughness in the EPMA measurement for the investigated films. The composition of all of the materials in Fig. 1 were normalized to the corresponding Cu at. % in the film. An exponential evolution of various Cu-poor phases has been apparent from the figure. For CuGaSe$_2$ films, with the composition around Z = 0, the figure shows the nearly stoichiometric composition of (1:1:2) (i.e., CuGaSe$_2$). However, with an increase in the Z-value, the composition of the films tends to deviate from the ideal stoichiometry and becomes closer to the composition of the ODC-phase, Cu$_4$Ga$_6$Se$_{11}$ (1:1.5:2.75) around Z = 0.30, and then to the Cu$_2$Ga$_5$Se$_8$ (1:1.67:3) when the Cu-deficiency parameter, Z, in the film approaches the value of 0.40. A further increase in the Z-value (Z ≈ 0.50) makes the composition of the film in good agreement with the ODC compound, Cu$_5$Ga$_4$Se$_{11}$ (1:2:3.5), and finally the composition approaches a close approximation of the Cu$_2$Ga$_5$Se$_8$ (1:3:5) phase, as seen for the film with Z ≈ 0.65, which is the largest Cu-deficient sample in this study. A polynomial fitting of the normalized composition shows another transition of the material to the (1:5:8) phase when Z approaches around 0.75. Conversely, for samples with Z < 0; the ratio, Ga/Cu < 1 suggests the deviation of the film from the stoichiometry to a more Cu-rich condition with excess Cu in the film.

Later, we plot the elemental composition of all the films on the Cu-Ga-Se ternary phase diagram (Fig. 2) as a function of their corresponding Cu-deficient parameter, Z. The composition of all of the films was found to lie along the Cu$_2$Se-Ga$_2$Se$_3$ pseudo binary tie line and no off-line composition was found in our study. Therefore, we can represent the composition of our studied samples along the pseudo binary line through the expression,

$$ (Cu_2Se)_x(Ga_2Se)_1-x $$

with $0 \leq x \leq 1$; $x$ being the ratio of Cu/(Cu + Ga). (1)

Along the Cu$_3$Se$_2$Ga$_2$Se$_3$ pseudo binary tie line, the composition of the samples around Z = 0 was found to reside on the stoichiometric (1:1:2) region, which is consistent with Fig. 1. Following the preceding equation, decreasing the bulk Cu/Ga ratio (i.e., increasing the Z-value) gradually moves the composition toward the Ga-rich region along the quasi-binary line through the structural transformation, thereby making various ODC phases dependent on the Cu-content in the film. We can explain the preceding phenomena as follows: due to its very low formation energy, the spontaneous formation of V$_{Cu}$ in the stoichiometric, and in the Cu-rich sample has been reported. Meanwhile, an increasing tendency of the Ga at. % with the increase of the Z-value has been observed in Fig. 1. Therefore, it is likely to generate Ga$_{Cu}$ antisite defects in Cu-poor CuGaSe$_2$ samples. Thus, the formation of a (2V$_{Cu}^{-1}$ + III$_{Cu}^{2+}$) defect pair is highly plausible in the Cu(In,Ga)Se$_2$ system due to their very low formation energy, as calculated with the first principle method by Zhang et al. According to them, a periodic spatial repetition of the m (m = 1 for the compound lies over the Cu$_2$Se-Ga$_2$Se$_3$ pseudo binary tie line in the Cu-Ga-Se phase diagram) unit of the (2V$_{Cu}^{-1}$ + III$_{Cu}^{2+}$) defect pair in each n = 4, 5, 6, 7, 8, 9, 10, and 11 units of the CuInSe$_2$ system gives rise to the formation of Cu$_m$In$_n$Se$_{8}$ (1:5:8), Cu$_3$In$_7$Se$_{12}$, Cu$_5$In$_7$Se$_{17}$, Cu$_7$In$_7$Se$_{22}$, and Cu$_9$In$_7$Se$_{27}$ defects, respectively, which they defined as ordered defect compounds (ODCs). However, since the Ga$_{Cu}$ antisite donor level in CuGaSe$_2$ is much deeper than the In$_{Cu}$ donor level in CuGaTe$_2$.
CuInSe₂ with respect to their corresponding conduction band minimum, the formation energy of \((2V_{\text{Cu}}^{-1} + In_{\text{Ga}}^{+2})\) in CuGaSe₂ is comparatively larger than that of \((2V_{\text{Cu}}^{-1} + In_{\text{Cu}}^{+2})\) in CuInSe₂. Therefore, it is difficult to form a \((1:3:5)\) phase in CuGaSe₂ at a near stoichiometric composition. Nevertheless, as the material becomes Cu-poor, thereby causing the Ga content to increase along the Cu₂-Se-Ga₃Se₅ tie line in the ternary phase diagram, the formation energy of this defect pair becomes lower, and even finally approaches negative values.\(^{5,11}\) Thus, the deficiency of the Cu content in the sample generates this defect along with other isolated defects such as Ga₅Cu, Cu-Se di-vacancy, etc., which eventually produce ODC-like phases. Our experimental finding is consistent with the theoretical calculation in Ref. \(^5\), where we have found a series of ODC phases by reducing the Cu-content in the bulk of our CuGaSe₂ films. The formation of secondary phases (ODCs) are also predicted for Ga ≥ 28 at.% (Z ≥ 0.3 in this study) according to the phase diagram of the Cu-Ga-Se system.\(^{12}\) Moreover, increases in the band-gap energy and a decrease of the majority carrier concentration in our CuGaSe₂ samples with the increase in the Z-value also suggest the formation of a defect-related ODC phase in the material.\(^{5,13,14}\)

To obtain structural evidence of the phase separation, we have performed synchrotron XRD of the several as-grown CuGaSe₂ thin films having different Z-values; this is shown in Fig. 3. As seen from the XRD profile, the (112) peak shifts from the position, \(2\theta = 27.6^\circ\), for the Cu-rich sample with \(Z = -0.13\) to the position, \(2\theta = 27.95^\circ\), for the Cu-deficient sample with \(Z = 0.63\). The systematic right shifting of the (112) peak with increasing Cu-deficiency in the film indicates the phase transition from the stoichiometric (1:1:2) phase to the ODC-related phases. The right shift of the peak can be attributed to the reduction of the lattice parameter in \((1:2.3.5), (1:3.5), \text{etc. ODC-related phases, comparing to that of the chalcopyrite structure.}^{15,16}\) This finding is consistent with results of several authors: a continuous decrease of the tetragonal unit cell parameter as a function of Cu-deficiency in the film has been reported for the Cu(In,Ga)Se₂ single crystal\(^{17}\) and also for physical vapor deposited Cu(In,Ga)Se₂ thin film.\(^{18}\) The reduction of the lattice parameter was attributed to the structural modification to more Cu-poor phases.

No peaks corresponding to the Cu₂-xSe phase was found in the investigated range of the XRD pattern for the Cu-excess film with \(Z < 0\). For the near stoichiometric film \((Z = 0.04)\), the XRD pattern reflects only the (1:1:2) chalcopyrite structure without evidence of any additional phases. However, an additional diffraction peak at \(2\theta \approx 22.8^\circ\) for the film with \(Z = 0.3\) and 0.63 can be attributed to the presence of the ODC-related phase.\(^{16}\) This additional reflection originates from the different cation ordering and the presence of Cu-vacancies in the ODC-related structures.\(^3\) Fitting of the (112) peak shows the co-existence of the (1:1:2) and (1:3:5) phases in the film with \(Z = 0.3\), while the contribution of the ODC phase in the XRD peak increases with the increase of the Z-value. The film with \(Z = 0.63\) shows the diffraction peaks that correspond to the almost single phase ODC (CuGa₅Se₈ phase) with no evidence of any (1:1:2) chalcopyrite phase in the structure. It should to be mentioned that the crystal structure of both CuGa₅Se₈ and CuGa₃Se₅ are almost similar, belonging to the same space group with almost similar lattice parameters and consequently, having a peak position at the same \(2\theta\) value in their corresponding X-ray diffraction profiles.\(^{15,16}\) Therefore, it is difficult to differentiate between these two phases from the XRD pattern. Consequently, the term ‘ODC-phase’ is applicable to both of these phases interchangeably in the discussion of x-ray diffraction results. No other less Cu-poor ODC phases (e.g., Cu₅In₉Se₁₆, Cu₃In₅Se₉, etc.) could be distinguished within the resolution limit of this measurement.

So far, we have seen the phase transition in various CuGaSe₂ samples in terms of the Cu-deficiency in the bulk of the corresponding film. Finally, to get a quantitative idea of the Cu-dependent phase transition along the depth of a similar film, we have used electron probe microanalysis of secondary phases with different accelerating voltages ranging from 2.5 to 20 kV. In EPMA, a characteristic x-ray spectrum is measured from the sample which is excited by a convergent electron beam irradiation. The intensity of the x-ray spectrum is compared with those of the references to determine the composition of the specimen. The primary electron energy induced by the electron accelerating voltage determines the penetration depth of the electron beam. Hence, the voltage dependence of the x-ray spectrum intensity reflects the composition depth distribution in the specimen. This principle can be used to identify other phases and to estimate their composition in the specimen. As the measured emission intensity is a weighted convolution of the entire probed depth, a parameter fitting of an analytical model using a computer was applied to deconvolute the measured spectra of accelerating voltage dependent data. Using this method, and considering a two-phase model, a surface phase segregated over the CuGaSe₂ films has been detected for several samples. The details of this model have been described elsewhere.\(^{19,20}\) An analysis of the as-grown samples with the Cu deficiency content, \(Z = 0.50\) and −0.13, has been shown in Figs. 4 and 5, respectively. The symbols in both of the figures show the composition of each material obtained through EPMA intensity measurement using a beam with a diameter of 50 μm. The solid line in the figures shows the fitting-result using the analytical model. To take

![FIG. 3. (Color online) Room temperature synchrotron x-ray diffraction pattern at the 0-2θ mode of several CuGaSe₂ thin films grown with different Cu-deficiency parameters, Z.](Image 84)


table I. Two-phase structure of several CuGaSe2 thin films, determined by the fitting of the elemental compositional data along the depth of the film, as measured by acceleration voltage dependent EPMA. Fitting was done based on a simple two-phase analytical model using WaveMetrics Igor Pro software. The compound shown next to the composition in the parentheses is the ODC phases which appear to be formed with this composition.

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<tr>
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<td>16:26:47 (∼Cu9Ga3Se12)</td>
<td>26.1:23.3:51.5</td>
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FIG. 4. Elemental data of CuGaSe2 thin films with the Cu-deficient parameter, Z = 0.50, determined by accelerated voltage dependent EPMA. All of the data were corrected by the ZAF model (see text). The solid line indicates the fitting-result using the two-phase analytical model.

FIG. 5. Elemental data of CuGaSe2 thin films with the Cu-deficient parameter, Z = −0.13, determined by accelerated voltage dependent EPMA. All of the data were corrected by the ZAF model (see text). The solid line indicates the fitting-result using the two-phase analytical model.

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pressure, it contributes to form the CuGaSe₂ film via several vapor-liquid-solid mechanisms.²⁵,²⁶ This growth mechanism can explain the relatively Cu-stoichiometric composition in the bulk of the film. However, the mechanism for the Cu-depleted surface formation even for the slightly Cu-rich bulk composition has not yet been understood. R. Herberholz et al.²⁷ presented a model, where the author described the formation of a Cu-poor surface in the Cu(In,Ga)Se₂ film, which was considered to be the consequence of positively charged donors on the surface and the migration of interstitial Cu (Cuᵢ) into the bulk from the surface. Therefore, finally, at the third stage of the growth procedure, when this quasi-liquid phase is exposed to the Ga vapor, the phase transition with the decrease in the bulk Cu-content creates Cu-va-
cency related defects which eventually act as a sink for the migrated Cu from the surface. Therefore, the phase transition on the surface is limited by the bulk Cu-content in the film. The order of the phase transition with the decrease in the Cu-content (i.e., increasing Z) follows the order as (Cu₂Ga₅Se₉) → (Cu₃Ga₇Se₁₂) → (CuGa₃Se₅) etc., along the Cu₂Se-Ga₅Se₃ quasi-binary line in the Cu-Ga-Se phase diagram.

IV. CONCLUSIONS

In conclusion, we have investigated the phase transition in a polycrystalline CuGaSe₂ thin film grown with various Cu-deficiency parameters, Z. A series of ODC phase formations were observed on the surface region and in the bulk of the film with an increasing Z-value. The evolution of the various ODC phases was confirmed by the EPMA data and the synchrotron x-ray diffraction method. Analysis of the compositional data along the various depths of the film, probed by accelerated voltage dependent EPMA, shows the presence of an extreme Cu-poor surface phase even in the CuGaSe₂ film with a stoichiometric bulk composition.

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