Cu-dependent phase transition in polycrystalline CuGaSe$_2$ thin films grown by three-stage process

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


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The Cu-dependent phase transition in polycrystalline CuGaSe₂ thin films has been studied by an 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. © 2011 American Institute of Physics. [doi:10.1063/1.3603022]

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 film. In particular, the formation of the Cu(In,Ga)₃Se₅, secondary phases, preferably segregated on the surface of the Cu₂Se-Ga₂Se₃ pseudo binary tie line is believed to have some positive impact on the low-gap-based device performance, mainly due to the bandgap widening and type inversion at the near-stoichiometric CuGaSe₂ film.

II. EXPERIMENTAL

Polycrystalline CuGaSe₂ thin films 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 × 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 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 Cu-deficiency parameters, Z [ = (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-analysis (EPMA) using a Shimadzu 8705 and Q-II system. The bulk Cu-deficiency parameter used in this study was calculated with the composition measured by EPMA at 15 kV. Synchrotron XRD was performed using Beam Line-4 C at E = 8.017 keV in KEK, Japan.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the elemental composition of several CuGaSe2 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 position of all of the materials in Fig. 1 were normalized to the EPMA measurement for the investigated films. The composition written along the vertical line gives rise to the formation of CuIn5Se8 (1:5:8), CuIn3Se5 (1:3:5), Cu3In5Se9 (1:1.67:3), Cu7In11Se20, and Cu4In6Se11 defect compounds (ODCs). However, since the GaCu antisite donor level in CuGaSe2 is much deeper than the InCu donor level in the Cu(In,Ga)Se2 system due to their very low formation energy, as calculated with the first principle method by Zhang et al.\textsuperscript{5,6} According to them, a periodic spatial repetition of the m (m = 1 for the compound lies over the Cu2Se-Ga2Se3 pseudo binary line in the Cu-Ga-Se phase diagram) unit of the CuInSe2 system gives rise to the formation of CuInSe8 (1:5:8), CuIn7Se12, CuIn6Se13, CuIn6Se16, CuIn5Se9 (1:1.67:3), Cu2In3Se20, and Cu4In6Se11 defect phases, respectively, which they defined as ordered defect compounds (ODCs). However, since the GaCu antisite donor level in CuGaSe2 is much deeper than the InCu donor level in

\begin{align*}
\text{(Cu}_2\text{Se})_{x}(\text{Ga}_2\text{Se}_3)_{1-x} \quad &\text{with } 0 \leq x \leq 1; \\
&\text{x being the ratio of Cu}/(\text{Cu} + \text{Ga}).
\end{align*}

Along the Cu3Se-Ga2Se3 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,

\begin{align*}
\text{(Cu}_2\text{Se})_{x}(\text{Ga}_2\text{Se}_3)_{1-x} \quad &\text{with } 0 \leq x \leq 1; \\
&\text{x being the ratio of Cu}/(\text{Cu} + \text{Ga}).
\end{align*}

Along the Cu3Se-Ga2Se3 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 VCu in the stoichiometric, and in the Cu-rich sample has been reported.\textsuperscript{9} 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 GaCu antisite defects in Cu-poor CuGaSe2 samples. Thus, the formation of a (2VCu\textsuperscript{1-} + III\textsuperscript{Cu\textsuperscript{2+}}) defect pair is highly plausible in the Cu(In,Ga)Se\textsubscript{2} system due to their very low formation energy, as calculated with the first principle method by Zhang et al.\textsuperscript{5,6}
CuInSe$_2$ with respect to their corresponding conduction band minimum, the formation energy of $(2V_{\text{Cu}}^{-1} + \text{Ga}_{\text{Cu}}^{1+})$ in CuGaSe$_2$ is comparatively larger than that of $(2V_{\text{Cu}}^{-1} + \text{In}_{\text{Cu}}^{1+})$ in CuInSe$_2$. Therefore, it is difficult to form a (1:3:5) phase in CuGaSe$_2$ at a near stoichiometric composition. Nevertheless, as the material becomes Cu-poor, thereby causing the Ga content to increase along the Cu$_2$Se-Ga$_3$Se$_5$ tie line in the ternary phase diagram, the formation energy of this defect pair becomes lower, and even finally approaches negative values. Thus, the deficiency of the Cu content in the sample generates this defect along with other isolated defects such as Ga$_{\text{Cu}}$-Cu-Se divacancy, 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 CuGaSe$_2$ films. The formation of secondary phases (ODCs) are also predicted for Ga $\geq$ 28 at. % $(Z \geq 0.3$ in this study) according to the phase diagram of the Cu-Ga-Se system. Moreover, increases in the band-gap energy and a decrease of the majority carrier concentration in our CuGaSe$_2$ samples with the increase in the Z-value also suggest the formation of a defect-related ODC phase in the material.

To obtain structural evidence of the phase separation, we have performed synchrotron XRD of the several as-grown CuGaSe$_2$ 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), etc. ODC-related phases, comparing to that of the chalcopyrite structure. This finding is consistent with results of several authors: a continuous decrease of the band-gap energy and a decrease of the majority carrier concentration results. No other less Cu-poor ODC phases (e.g., Cu$_2$In$_5$Se$_{16}$, Cu$_3$In$_5$Se$_9$, etc.) could be distinguished within the resolution limit of this measurement.

So far, we have seen the phase transition in various CuGaSe$_2$ 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 CuGaSe$_2$ films has been detected for several samples. The details of this model have been described elsewhere. 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 $\mu$m. The solid line in the figures shows the fitting-result using the analytical model. To take
Cu$_{2-x}$Se. For the near-stoichiometric film with $Z$ which is supposed to form some Cu-rich phases, e.g., CuGaSe$_2$ films were determined as listed in Table I. In our study a two times iteration was used during the calculation that makes it ZAF2 correction model. After fitting to each elemental data under an equal depth condition, and using the technique described in the preceding text, the surface and bulk compositions of several CuGaSe$_2$ films were determined as listed in Table I.

A systematic evolution of phases on the surface region was observed when bulk Cu-content in the films was varied, as seen in Table I. While maintaining a stoichiometric (1:1:2) composition on the surface, an excess amount of Cu was observed in the bulk region of the film with $Z = -0.13$, which is supposed to form some Cu-rich phases, e.g., Cu$_{2-x}$Se. For the near-stoichiometric film with $Z \approx 0$, a few nm thin Cu-depleted layers (Cu$_3$Ga$_5$Se$_9$) were found to exist over the slightly Cu-rich (1:1:2) bottom phase. For the Cu-poor film with $Z = 0.50$, the Cu-poor bulk phase (CuGa$_2$$_{1.5}$Se$_{3.5}$) was found to be covered by a more pronounced Cu-poor CuGa$_3$Se$_5$ (1:3:5) surface phase. These findings have two major implications: first, with the increase in the bulk $Z$-value (i.e., a decrease of the Cu-content) in the film, the structural modification allows not only the surface, but also the bulk of the film, i.e., the whole composition is to be transformed to the ODC compound; second, there is a phase transition along the depth of the similar film making the surface region more Cu-poor compared to the bulk of the film. Consequently, if we decrease the bulk Cu-content in several CuGaSe$_2$ films, the structural transformation to a more Cu-poor phase will appear more rapidly at the surface region than that of the bulk region of the various films. It also suggests that the phase transition starts at the surface region of the films and then proceeds toward the direction of the bulk region. The above findings also confirm the presence of the Cu-depleted ODC phase (although not the pronounced Cu-poor CuGa$_3$Se$_5$ phase) over the extreme surface of the bulk region. 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Cu-Se binary phase diagram.\(^\text{24}\) Cu-Se can exist as quasi-liquid form at the growth temperature of \(~520\) °C at the second stage. Therefore, finally, at the third stage of the growth procedure, when this quasi-liquid phase is exposed to the Ga and Se fluxes under the environment of sufficient Se vapor pressure, it contributes to form the CuGaSe\(_2\) film via several vapor-liquid-solid mechanisms.\(^\text{25,26}\) 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 \textit{et al}.\(^\text{27}\) presented a model, where the author described the formation of a Cu-poor surface in the Cu(In,Ga)Se\(_2\) film, which was considered to be the consequence of positively charged donors on the surface and the migration of interstitial Cu (Cu\(_{i}\)) into the bulk from the surface. Thus, considering the above phenomena, we can consider a model where the stoichiometric bulk phase is covered by a thin Cu-depleted ODC layer. This Cu-depleted phase (e.g., Cu\(_2\)Ga\(_5\)Se\(_9\)) on the surface region proceeds along the depth of the sample toward the bulk region until the structural transformation allows the transition to a more pronounced Cu-poor phase (e.g., CuGa\(_3\)Se\(_5\)) with the further decrease of the bulk Cu-content during growth. According to the model of Herberholz \textit{et al}., a further decrease of the Cu-content in the bulk creates Cu-vacancy related defects which eventually act as a sink for the migrated Cu\(_{i}\) 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 (Cu\(_2\)Ga\(_5\)Se\(_{11}\)) \(\rightarrow\) (Cu\(_2\)Ga\(_5\)Se\(_9\)) \(\rightarrow\) (Cu\(_2\)Ga\(_5\)Se\(_7\)) \(\rightarrow\) (Cu\(_2\)Ga\(_5\)Se\(_{12}\)) \(\rightarrow\) (CuGa\(_3\)Se\(_5\)) \(\rightarrow\) (CuGa\(_3\)Se\(_5\)) etc., along the Cu\(_2\)Se-Ga\(_2\)Se\(_3\) quasi-binary line in the Cu-Ga-Se phase diagram.

IV. CONCLUSIONS

In conclusion, we have investigated the phase transition in a polycrystalline CuGaSe\(_2\) 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 CuGaSe\(_2\) film with a stoichiometric bulk composition.

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