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

M. M. Islam,[1,a),b)] A. Yamada,[2] T. Sakurai,[1] M. Kubota,[3] S. Ishizuka,[2] K. Matsubara,[2] S. Niki,[2] and K. Akimoto[1]

[1]*Institute of Applied Physics, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan*
[2]*Research Center for Photovoltaics, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8568, Japan*
[3]*Photon Factory, IMSS, High Energy Accelerator Research Organization (KEK), 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan*

The Cu-dependent phase transition in polycrystalline CuGaSe$_2$ 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 Cu$_2$Se-Ga$_2$Se$_3$ pseudo binary tie line was found to shift from the stoichiometric CuGaSe$_2$ (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 CuGaSe$_2$ film has been investigated by the synchrotron x-ray diffraction method. The existence of the Cu-poor surface phase over the near-stoichiometric bulk CuGaSe$_2$ 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)Se$_2$ (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.[1] 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)$_3$Se$_5$, Cu(In,Ga)$_2$Se$_{3.5}$, etc., phases on the surface of the slightly Cu-poor film and also in the stoichiometric film is a commonly observed phenomenon in CIGS material grown by various methods[2,3] and 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 surface. In these secondary phases, the vacancies might orderly occupy particular crystallographic sites in the structure to satisfy the four electrons per site rule. For this reason they are usually called ordered vacancy compounds.[4] These compounds are also referred to as ordered defect compounds (ODCs) by Zhang *et al.*, where they explained that these compounds stem from the repetition of the defect pair, $[2V_{Cu}^{-1} + (In,Ga)_{Cu}^{+2}]$ in an orderly fashion in the Cu(In, Ga)Se$_2$ system.[5,6] However, no such evidence of the ODC phase formation has been reported for the stoichiometric CuGaSe$_2$-based material, the wide gap counter part of CuInSe$_2$, which is considered as a suitable candidate for the realization of the high efficiency solar cell and also for the top or middle cell of the tandem device, based on the CIGS material.[7] Therefore, an intensive study becomes indispensa-

ble to understand the proper physics and growth conditions for the ODC phase formation in this material. In this study, we have systematically grown several CuGaSe$_2$ thin films by changing the Cu content in the bulk of the film. A Cu-deficiency parameter, Z, which is defined as the $Z = (1 - Cu/Ga)$, has been used to determine the deviation of the film from the stoichiometric CuGaSe$_2$ (1:1:2) composition. Thus, with an increase in the Z-value, the sample becomes more Cu-poor and Ga-rich while for $Z < 0$, the sample becomes Cu-rich. In this report we focus on the investigation of the evolution of various Cu-poor phases in CuGaSe$_2$ thin films as a function of the Cu-deficiency parameter, Z. The phase transition along the depth of the CuGaSe$_2$ samples has also been studied.

II. EXPERIMENTAL

Polycrystalline CuGaSe$_2$ thin films with the typical thickness of 2 μm were grown over Mo-coated soda lime glass substrates through a three-stage co-evaporation process using a molecular beam epitaxy system.[8] 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, 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 CuGaSe$_2$ films with various bulk 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

a)Electronic mail: monirul@mbe.rcast.u-tokyo.ac.jp.
b)Present address: Research Center for Advanced Science and Technology (RCAST), The University of Tokyo, 4-6-1 Komaba, Meguro-Ku, Tokyo-153-8904, Japan.

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 $CuGaSe_2$ 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, $Cu_4Ga_6Se_{11}$ (1:1.5:2.75) around Z = 0.30, and then to the $Cu_3Ga_5Se_9$ (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, $Cu_2Ga_4Se_7$ (1:2:3.5), and finally the composition approaches a close approximation of the $CuGa_3Se_5$ (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_2Se-
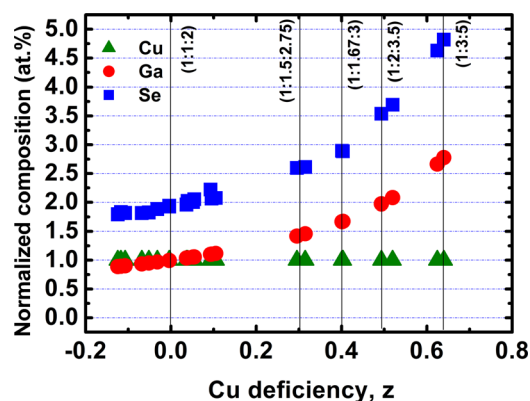

FIG. 1. (Color online) Composition of various $CuGaSe_2$ thin films as a function of the Cu-deficiency parameter, Z. All of the compositions are normalized to Cu at. % in the films. The composition written along the vertical line represents various ODC phases.
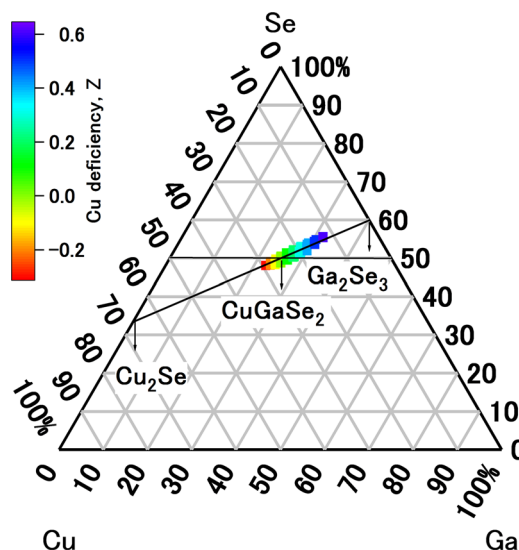

FIG. 2. (Color online) Composition of various $CuGaSe_2$ films plotted on the Cu-Ga-Se ternary phase diagram as a function of the Cu-deficient parameter, Z. The composition of all of the films lies on the Cu_2Se-Ga_2Se_3 pseudo binary tie line.

Ga_2Se_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,

$$(Cu_2Se)_x(Ga_2Se_3)_{1-x} \quad \text{with} \quad 0 \le x \le 1;$$
$$\text{x being the ratio of } Cu/(Cu + Ga). \tag{1}$$

Along the Cu_2Se-Ga_2Se_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.[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 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.*[5,6] According to them, a periodic spatial repetition of the m (m = 1 for the compound lies over the Cu_2Se-Ga_2Se_3 pseudo binary tie line in the Cu-Ga-Se phase diagram) unit of the $(2V_{Cu}^{-1} + In_{Cu}^{+2})$ 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 $CuIn_5Se_8$ (1:5:8), $CuIn_3Se_5$ (1:3:5), $Cu_3In_7Se_{12}$, $Cu_2In_4Se_7$ (1:2:3.5), $Cu_5In_9Se_{16}$, $Cu_3In_5Se_9$ (1:1.67:3), $Cu_7In_{11}Se_{20}$, and $Cu_4In_6Se_{11}$ defect phases, 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

$CuInSe_2$ with respect to their corresponding conduction band minimum, the formation energy of $(2V_{Cu}{}^{-1} + Ga_{Cu}{}^{+2})$ in $CuGaSe_2$ is comparatively larger than that of $(2V_{Cu}{}^{-1} + In_{Cu}{}^{+2})$ in $CuInSe_2$.[10] 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_2Se-Ga_2Se_3 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 Ga_{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.[12] 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.[6,13,14]

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, $2\theta = 27.6^o$, for the Cu-rich sample with $Z = -0.13$ to the position, $2\theta = 27.95^o$, 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.[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 $Cu(In,Ga)Se_2$ single crystal[17] and also for physical vapor deposited $Cu(In, Ga)Se_2$ thin film.[18] The reduction of the lattice parameter was attributed to the structural modification to more Cu-poor phases.
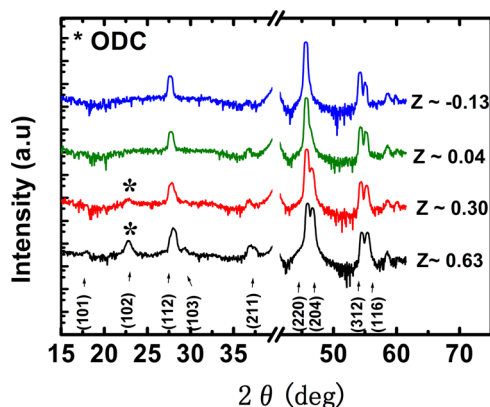

FIG. 3. (Color online) Room temperature synchrotron x-ray diffraction pattern at the θ-2θ mode of several $CuGaSe_2$ thin films grown with different Cu-deficiency parameters, Z.

No peaks corresponding to the $Cu_{2-x}Se$ 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 $2\theta \approx 22.8^o$ 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 ($CuGa_3Se_5$ 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 $CuGa_2Se_{3.5}$ and $CuGa_3Se_5$ are almost similar, belonging to the same space group with almost similar lattice parameters and consequently, having a peak position at the same 2θ 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., $Cu_5In_9Se_{16}$, $Cu_3In_5Se_9$, 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.[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
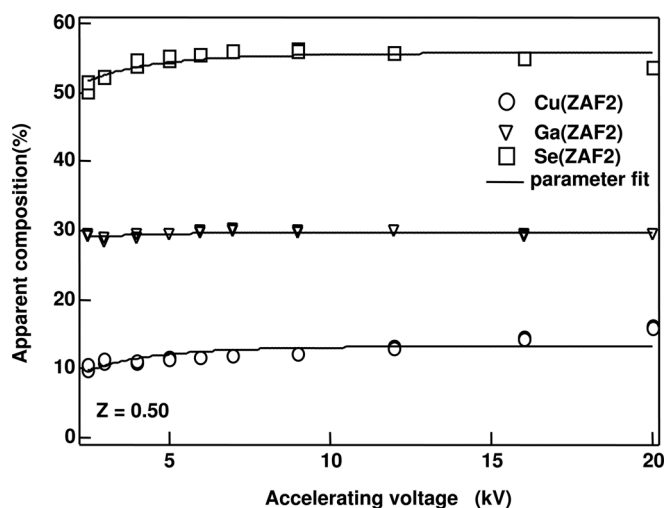
FIG. 4. Elemental data of CuGaSe$_2$ thin films with the Cu-deficient parameter, Z = 0.50, determined by accelerated voltage dependent EPMA. All of the data were corrected by the ZAF model (see text). The solid line indicates the fitting-result using the two- phase analytical model.

into account the surface roughness effect in our EPMA measurement, the composition data were corrected using the ZAF model.[21] This model considers atomic number (Z), absorption (A) and fluorescence (F) of the specimen to make correction of the EPMA data. 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.[22] For the near-stoichiometric film with Z ∼ 0, a few
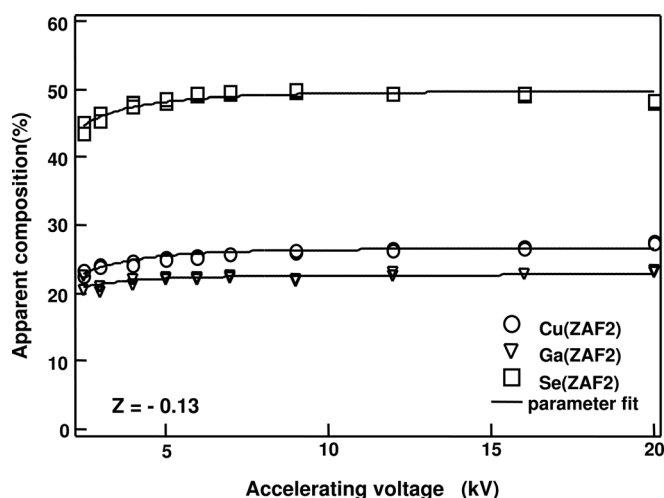

FIG. 5. Elemental data of CuGaSe$_2$ thin films with the Cu-deficient parameter, Z = −0.13, determined by accelerated voltage dependent EPMA. All of the data were corrected by the ZAF model (see text). The solid line indicates the fitting-result using the two- phase analytical model.

TABLE I. Two-phase structure of several CuGaSe$_2$ 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.

Z = (1 − Cu/Ga)	Surface composition [Cu]:[Ga]:[Se]	Bulk composition [Cu]:[Ga]:[Se]
0.50	9:29:51 ($\approx$CuGa$_3$Se$_5$)	14.2:29.9:56.1 ($\approx$CuGa$_{2.1}$Se$_{3.95}$)
0.01	16:26:47 ($\approx$Cu$_3$Ga$_5$Se$_9$)	26.1:23.3:51.5
−0.04	16:24:46 ($\approx$Cu$_4$Ga$_6$Se$_{11}$)	26.4:23.5:51.3
−0.13	20:19:41 ($\approx$CuGaSe$_2$)	27.3:23.0:50.1

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$_{2.1}$Se$_{3.95}$) [$\cong$ (Cu$_3$Ga$_7$Se$_{12}$)] 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 it is not the pronounced Cu-poor CuGa$_3$Se$_5$ phase) over the extreme surface of the CuGaSe$_2$ thin film, even for near stoichiometric and slightly Cu-rich bulk composition, although any structural evidence of the ODC phase was not perceptible from the synchrotron x-ray diffraction profile. Of course, the degree of the Cu-depletion strictly depends on the order of the Cu-deficiency at the bulk region of the film. The presence of the Cu-depleted surface layer has already been detected by the modeling of the grazing incidence x-ray diffraction for the polycrystalline Cu(In,Ga)Se$_2$ thin film[18] and also for the Cu(In,Ga)Se$_2$ powder compound,[17] as evidenced by the x-ray photoemission spectroscopy study. Therefore, the Cu-poor surface region appears to be a general phenomenon in CIGS-based material.

However, to explain the compositional inhomogeneities along the depth of the film, we consider the growth procedure of our CuGaSe$_2$ samples. In the three-stage growth system, the Cu and Se material were co-evaporated at the second stage of the growth process. To obtain overall improved electrical properties with large grain size, Cu and Se were evaporated until Cu/III in the film becomes 1.3 at the end of the second stage.[23] Under this Cu-rich condition, excess Cu segregates in the form of Cu-Se phases on the surface of the film along the growth direction. According to the

Cu-Se binary phase diagram,[24] Cu-Se can exist as quasi-liquid form at the growth temperature of $\sim$520 °C at the second stage. Therefore, finally, at the thirdstage of the growth procedure, when this quasi-liquid phase is exposed to the Ga and Se fluxes under the environment of sufficient Se vapor pressure, it contributes to form the CuGaSe$_2$ film via several vapor-liquid-solid mechanisms.[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)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$_3$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 *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$_4$Ga$_6$Se$_{11}$) $\rightarrow$ (Cu$_3$Ga$_5$Se$_9$) $\rightarrow$ (Cu$_2$Ga$_4$Se$_7$) $\rightarrow$ (Cu$_3$Ga$_7$Se$_{12}$) $\rightarrow$ (CuGa$_3$Se$_5$) $\rightarrow$ (CuGa$_5$Se$_8$) 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.

[1] I. Repins, M. A. Contreras, B. Egaas, C. DeHart, J. Scharf, C. L. Perkins, B. To, and R. Noufi, Prog. Photovoltaics **16**, 235 (2008).
[2] A. J. Nelson, J. R. Tuttle, R. Noufi, D. Rioux, R. Patel, and H. Hochst, J. Appl. Phys. **74**, 5757 (1993).
[3] J. R. Tuttle, D. S. Albin, and R. Noufi, Sol. Cells **30**, 21 (1991).
[4] G. Marin, J. M. Delgado, S. M. Wasim, C. Rincón, G. S. Perez, A. E. Mora, P. Bocaranda, J. A. Henao, J. Appl. Phys. **87**, 7874 (2000).
[5] S. B. Zhang, S.-H. Wei, and A. Zunger, Phys. Rev. Lett. **78**, 4059 (1997).
[6] S. B. Zhang, S. H. Wei, A. Zunger, H. Katayama-Yoshida, Phys. Rev. B **57**, 9642 (1998).
[7] S. Nishiwaki, S. Siebentritt, P. Walk, and M. Ch. Lux-Steiner, Prog. Photovoltaics **11**, 243 (2003).
[8] K. Sakurai, R. Hunger, N. Tsuchimochi, T. Baba, K. Matsubara, P. Fons, A. Yamada, T. Kojima, T. Deguchi, H. Nakanishi, and S. Niki, Thin Solid Films **431–432**, 6 (2003).
[9] T. Maeda and T. Wada, J. Phys. Chem. Solids **66**, 1924 (2005).
[10] S.-H. Wei, S. B. Zhang, and A. Zunger, Appl. Phys. Lett. **72**(24), 3199 (1998).
[11] J. F. Guillemoles, Thin Solid Films **361-362**, 338 (2000).
[12] J. C. Mikkelsen, J. Electron. Mater. **10**, 541 (1981).
[13] G. E. H. M. Ariswan, M. Abdelali, F. Guastavino, and C. Llinares, Solid State Commun. **124**, 391 (2002).
[14] C. Rincón, S. M. Wasim, and G. Marín, Appl. Phys. Lett. **80**, 998 (2002).
[15] W. Honle, G. Kuhn, and U. C. Boehnke, Cryst. Res. Technol. **23**, 1347 (1988).
[16] G. Marin, S. Tauleigne, S. M. Wasim, R. Guevara, J. M. Delgado, C. Rincón, A. E. Mora, G. S. Pérez, Mater. Res. Bull. **33**, 1057 (1998).
[17] M. Souilah, A. Lafond, C. Guillot-Deudon, S. Harel, and M. Evain, J. Solid State Chem. **183**, 2274 (2010).
[18] I. M. Kötschau and H. W. Schock, J. Phys. Chem. Solids **64**, 1559 (2003).
[19] A. Yamada, P. J. Fons, S. Nik, and H. Oyangi, Jpn. J. Appl. Phys. **38**, 96 (1999).
[20] A. Yamada, P. Fons, K. Matsubara, K. Iwata, K. Sakurai, and S. Niki, Thin Solid Films **431–432**, 277 (2003).
[21] J. Philibert and R. Tixier, *Quantitative Electron Probe Microanalysis* (National Bureau of Standards Special Publication, Gaitherburg, 1968).
[22] P. Fons, S. Niki, A. Yamada, and H. Oyanagi, J. Appl. Phys. **84**, 6296 (1998).
[23] R. Caballero, S. Siebentritt, K. Sakurai, C. A. Kaufmann, H. W. Schock, and M. Ch. Lux-Steiner, Thin Solid Films **515**, 5862 (2007).
[24] T. B. Massalski, H. Okamoto, P. R. Subramanian, and L. Kacprzak, *Binary Alloy Phase Diagram* (ASM International, Metals Park, OH, 1990).
[25] J. R. Tuttle, M. Contreras, M. H. Bode, D. Niles, D. S. Albin, R. Matson, A. M. Gabor, A. Tennan, A. Duda, and R. Noufi, J. Appl. Phys. **77**, 153 (1995).
[26] S. Nishiwaki, N. Kohara, T. Negami, H. Miyake, and T. Wada, Jpn. J. Appl. Phys. **8**, 2888 (1999).
[27] R. Herberholz, U. Rau, H. W. Schock, T. Haalboom, T. Gödecke, F. Ernst, C. Beilharz, K. W. Benz, and D. Cahen, Eur. Phys. J.: Appl. Phys. **6**, 131 (1999).