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# Synchrotron XRD study of the $CuGaSe_2$ thin films grown with various Cu/III ratio

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## 1 Introduction

Chalcopyrite $Cu(In,Ga)Se_2$ (CIGS), is one of the most promising materials to realize high-efficiency, low cost thin film solar cell. Efficiency of 19.9% has already been achieved for the CIGS-based solar cell [1]. Deviation from the ideal stoichiometry (i.e. 1:1:2) of this material is reported to form some secondary phases e.g. $Cu(In,Ga)_3Se_5$ (1:3:5), $Cu(In,Ga)_2Se_{3.5}$ (1:2:3.5) etc. which are commonly named as ordered defects compounds (ODC) preferably segregated on the surface of the film and affect electrical, optical and microstructural properties of the films.Therefore, intensive study is indispensable to understand the proper physics and growth condition for the ODC phase formation in this material. In this study we have performed synchrotron XRD of the $CuGaSe_2$ thin film to investigate the formation of ODC phase in our samples.

## 2 Experiment

Polycrystalline $CuGaSe_2$ thin films with the typical thickness of 2 μm were grown over Mo-coated soda lime glass (SLG) substrates through a three-stage co-evaporation process using molecular beam epitaxy system [8]. All the samples were grown at the constant flux rate of Cu, Ga and Se. Several $CuGaSe_2$ films with various Cu/III(= Cu/(Cu+Ga) ratio have been fabricated by changing the third stage growth time. Synchrotron XRD was performed using Beam Line-4C at E= 8.017 keV in KEK, Japan.

## 3 Results and Discussion

Figure 1 shows synchrotron XRD of the several $CuGaSe_2$ thin films having different Cu/III ratio in the film. As seen from the XRD profile, the (112) peak shifts from $2\theta = 27.6^o$ for Cu-rich sample with Cu/III = 1.12 to $2\theta = 27.95^o$ for the Cu-deficient sample with Cu/III = 0.37. The systematic right shifting of (112) peak with increasing Cu-deficiency in the film indicates the phase transition from the stoichiometric (1:1:2) phase to the ordered defect chalcopyrite (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 phases comparing to that of (1:1:2) chalcopyrite structure [2]. No peak related to the formation of $Cu_{2-x}Se$ phases was found in the investigated range of XRD pattern for the Cu-excess film with Cu/III = 1.12.

For the film with composition near stoichiometry (Cu/III ~ 1.0), XRD pattern reflect only (1:1:2) chalcopyrite structure without any additional phase formation. However, an additional peak appeared at $2\theta \approx 22.8^o$ for the film with Cu/III ~ 0.7 and 0.37, which can be attributed to the formation of ODC related phase. This additional reflection originates from the different cation ordering and the presence of Cu-vacancies in the ODC related structures. Fitting of the (112) peak shows the co-existing of both chalcopyrite (i.e. 1:1:2) and ODC (i.e. 1:3:5) phase in this film. Further reduction of Cu/III ratio increases the contribution of ODC phase as can be seen for the film with Cu/III ~ 0.37 where, the XRD patterns could attributed to (1:3:5) phase only with no evidence of (1:1:2) chalcopyrite phase. These results suggest that reduction of Cu/III ratio in the $CuGaSe_2$ films introduce phase transition from the stoichiometric to the ODC phases that affect the solar cell performances fabricated based on this material and the optimization of this phase transition is necessary to realize the best efficiency.

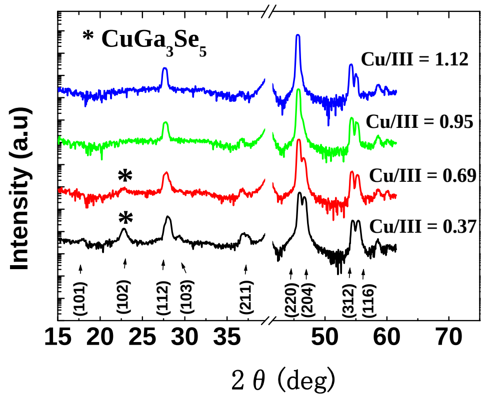


*Fig. 1* Synchrotron X-ray diffraction pattern at θ-2θ mode of several $CuGaSe_2$ thin films grown with different Cu/III ratio in the film.

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## References

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